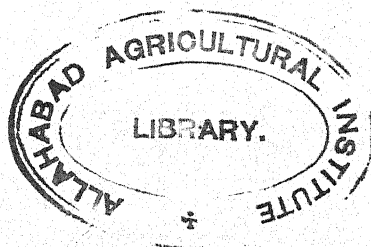


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## EVAPORATION FROM A PLAIN WATER SURFACE.

BY

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*Imperial Agricultural Chemist.*

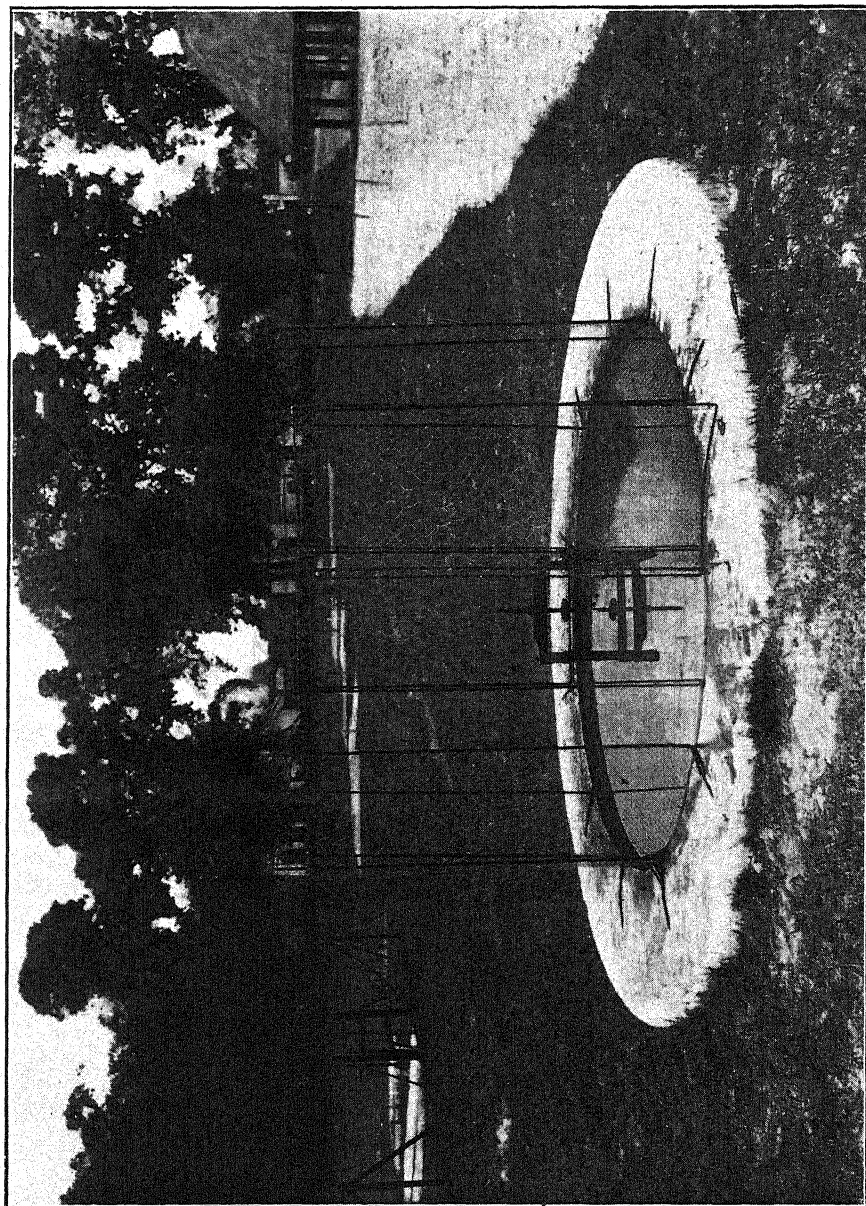
IN connection with the records of the water requirements of crops which have been maintained here during the past few years, information as to the amount of water which evaporates from a plain water surface in India was desired. Enquiry showed, however, that the amount of such information was very limited. The Meteorological Department was able to supply data from the Madras Observatory (see page 15). Another record obtained from Roorkee was obviously inexact because the evaporation found during the hot months was not greater than for the cold weather. Other records were being maintained by the Irrigation Department, Punjab (see page 15), but these were not then available, and in any case would be of doubtful service for Behar.

*The Tank.*—It was accordingly decided to maintain a record at Pusa. For this purpose a cement-lined masonry tank was constructed of the following dimensions: diameter 6 ft. 6 in. by depth 5 ft. It was situated in a field, but was not as free from neighbouring trees as might be desired; there is a line of bamboos about 110 ft. on the west side, and an avenue of teaks on the south-east side is 100 ft. distant. This position of the tank was dictated by the fact that difficulties would arise in preventing such a tank from being interfered with if it were placed in any large open field, whereas in the compound of the pot-culture house the necessary protection was available.

*The Evaporimeter.*—The first instrument employed for maintaining the record was a self-recording evaporimeter made by one of the larger meteorological instrument makers, and consisted essentially of two parts: (a) a float which was suspended by a metal cord from a pulley which actuated a pen through toothed gearing, and (b) a rotating drum which carried the paper chart on which the curve would be drawn. The instrument proved defective for two reasons. First, a part of the mechanism was exposed to the outside atmosphere, and dust rapidly collected in the toothed gearing. It would be quite impossible to prevent the dust of the Indian atmosphere outside from obtaining access to such instruments however carefully enclosed they might be. The gearing became gradually blocked, which affected the pen, and the record accordingly was soon defective. The second defect lay in the fact that the scale reading on the chart only indicated 2 mm. for each line, and the evaporation could only be estimated approximately to the nearest .5 mm. As will be subsequently seen, it is necessary to be able to estimate the evaporation to .1 mm. per 24 hours in order to demonstrate properly the magnitude of this quantity.

This experience with an otherwise well constructed self-recording evaporimeter led me to reject any further attempts in the use of such instruments. At this time a description was published in "Punjab Irrigation Branch Paper" No. 11, Part I A, page 44, of the instrument which was being employed in the Punjab for their records, and the Chief Engineer very kindly supplied me with one of these. It consists of an iron rod which stands vertically on an iron foot in the tank. The rod has a screw thread and on this a small hand wheel works. There is also a pointer which travels along the rod in a groove and this travels upwards and downwards with the hand wheel. Thus it can be brought carefully into contact with the water surface and its position in respect of some zero point ascertained. For the Pusa tank this instrument was slightly altered; the foot with a part of the rod was cut off, and the portion carrying the pointer was fixed, as seen in the Plate I, to an iron frame over the water

PLATE I.



EVAPORIMETER AND TANK.





surface. Also the small hand wheel was divided into tenths on the periphery. In order to ascertain the position of the water surface, it is only necessary to screw the pointer carefully down to the water surface, and then to count the revolutions from this position back to the zero. For the zero point a small iron stud was fixed into the pointer groove. Each revolution of the hand wheel = .298 cm., and since the position of the water surface can be read to  $\frac{1}{20}$  part of this (= .015 cm.), the instrument forms, in so far, a very exact measure of its position.

*Protection of the tank.*—At first the tank was left quite exposed, but in 1910 it was decided to surround it with a guard of wire netting. A ring of dry earth placed round the tank showed that animals, presumably jackals, came at night and drank water from the tank. The number of such was not large. For example, the following counts were made :—

On 26th May 1910—foot prints of two or three jackals.

On 27th May 1910—foot prints of two jackals.

On 28th May 1910—none.

On 29th May 1910—foot prints of one large and one small jackal.

On 30th May 1910—foot prints of one jackal.

On 31st May 1910—foot prints of one jackal.

On 1st June 1910—none.

On 2nd June 1910—foot prints of one jackal.

On 3rd June 1910—foot prints of one or two jackals.

On 4th June 1910—none.

The quantity of water which was being thus taken was not sufficient to materially affect the record, but since it was a measurable error, wire netting was fixed on the rim. The netting is 4 ft. high and of 2 in. mesh, and in addition a second strip of  $\frac{1}{2}$  in. mesh by 12 in. high was fixed at the bottom. The former prevents any large animals from drinking whilst the latter keeps off small ones. The mesh was as large as possible so as to interfere with the wind as little as might be.

*Percolation through walls of tank.*—The loss of water due to percolation through the sides and bottom of the tank has



been determined several times. Since it was cement lined, the anticipation was that it would prove only fairly water-proof. The first test was made by covering the top of the tank with 1 in. planks which fitted fairly well together, and whilst not entirely excluding evaporation, would nevertheless reduce it so much that an estimate of the amount of percolation would be possible. An aperture was left for the pointer to pass on to the water surface. This mode of stopping evaporation proved highly defective. The timber became wet and warped badly and most irregular readings were obtained. Another method which has proved entirely satisfactory is to pour a layer of mustard oil about .3 cm. thick over the water surface. Since vegetable oil is substantially not volatile at ordinary temperatures, it follows that any fall in the surface would be occasioned only by percolation of the water through the sides and bottom of the tank. Tests were made in 1911 and in 1913. The following are the records:—

1911.			1913.		
Gauge reading.			Gauge reading.		
November 13th	...	9.2	February 17th	...	2.7
" 14th	...	9.2	" 18th	...	2.7
" 15th	...	9.25	" 19th	...	2.7
" 16th	...	9.25	" 20th	...	2.7
" 17th	...	9.25	" 21st	...	2.7
" 18th	...	9.25			
" 19th	...	9.25			

The variation is therefore less than  $1/20$  revolution of the hand wheel, that is,  $< .015$  cm. in 5 days and is therefore negligibly small.

*Rim of tank.*—One defect in the construction of the tank should be noticed. The rim is horizontal. As a consequence any rain which falls may in part run into the tank, in part away from it. This could have been obviated by giving the rim a slope, either inwards or outwards, but this was not done because in either case air movements over the water surface would be interfered with. Constructed as it is the water surface is maintained within about 1" of the surrounding ground level. Thus

the water surface during dry weather has been exposed more normally than if a bevelled rim has surrounded it, but any rainfall renders the estimation of the evaporation impossible.

*Mode of maintaining the record.*—In using the instrument the procedure has been to read the position of the pointer at 8 A.M. daily; next to remove any leaves which may have blown into the tank; then to add sufficient water to bring the surface to within about 1" of the rim and again to record its level; the reading of the gauge at 8 A.M. the next morning before adding water, yields, when subtracted from that of the previous day (after addition of water), the amount of water which has evaporated in 24 hours. The actual record is naturally in terms of revolutions of the hand wheel in the first place, which is then converted into millimetres.

*Data obtained.*—Since there is so little published information on the subject of evaporation in India, the complete data for the years 1911 and 1912 are set out as Statement I. From these, averages have been taken for (a) a monthly estimate of the daily evaporation, Statement II, and (b) the curves which are published as Charts I & II.

Recently the monthly averages of evaporation at Lyallpur in the Punjab have been published in "Irrigation Branch Paper" II-C, and these are added to Statement II. As published in Paper II-C, the data are expressed in terms of feet per hour, and this form has been converted into mm. per 24 hours so as to be comparable with our data. Also the means of the Madras record, for the years 1898-1903, have been converted from inches per day to mm. per 24 hours and added to Statement II.

An examination of the columns in this statement shows that the rate of evaporation during the cold weather months is much the same at Pusa and at Lyallpur, but that it is much higher at Lyallpur throughout the six hot months from May to October. At Madras there is a much smaller annual variation as might be expected. At Pusa during the hottest months the rate is three times that of the coldest; at Lyallpur it is five times; but at Madras the rate does not rise to twice.

## EVAPORATION FROM A PLAIN WATER SURFACE.

CHART I.

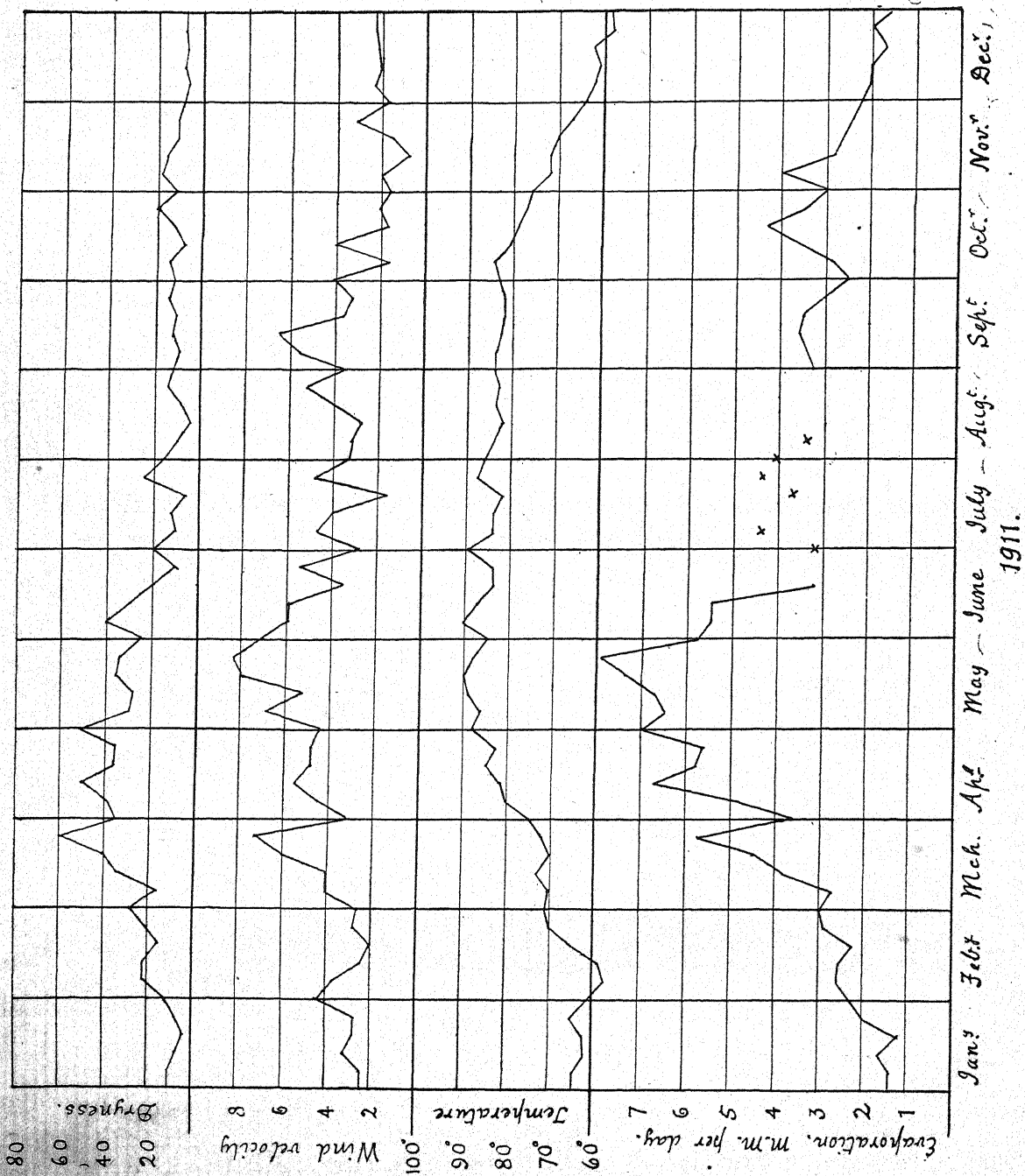
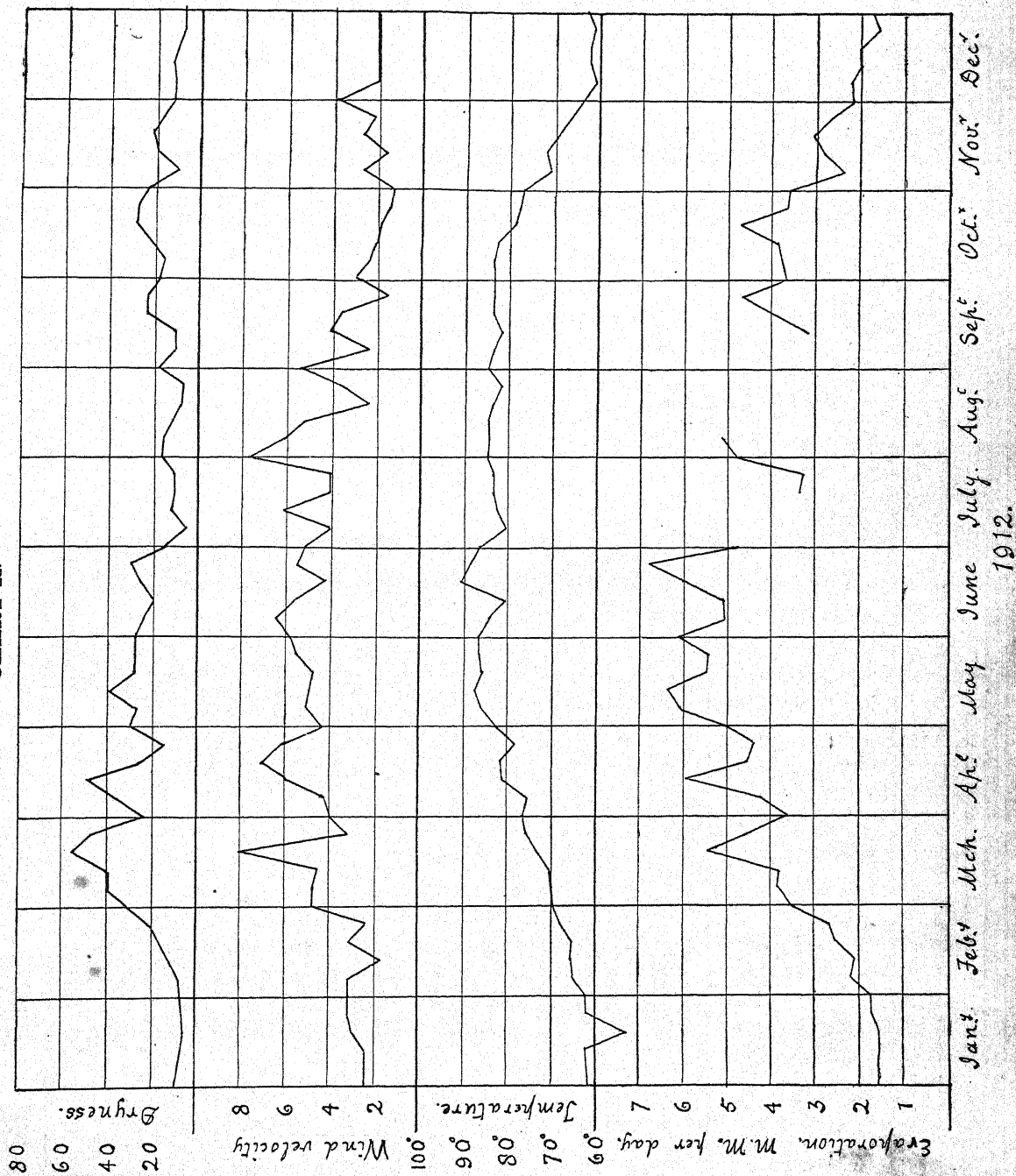


CHART II.





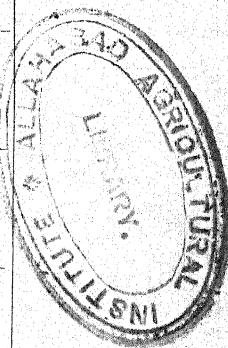
STATEMENT I.  
*Evaporation from a plain water surface at the Agricultural Research Institute, Pusa (1911).*

Date.	January.*	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	Dec.
1st	1.8	2.4	2.1	3.3	6.6	3.3	4.8	rainy day	rainy day	2.4	3.3	2.1
2nd	1.2	2.7	rainy day	3.6	6.0	5.7	rainy day	3.6	rainy day	2.4	3.6	1.5
3rd	1.2	3.3	2.1	4.2	4.8	6.9	4.5	rainy day	"	3.0	4.5	2.1
4th	1.9	2.7	2.7	4.8	9.8	6.3	3.9	3.3	"	3.9	5.7	1.8
5th	1.5	2.4	3.3	6.3	6.0	rainy day	rainy day	rainy day	4.2	rainy day	3.6	2.1
6th	1.8	2.7	3.6	6.9	6.6	"	"	rainy day	3.0	"	3.0	2.7
7th	2.1	2.7	3.0	5.4	7.2	"	"	"	rainy day	"	2.7	2.1
8th	1.5	2.7	5.4	5.1	6.0	"	"	"	3.0	"	3.0	2.1
9th	1.5	2.1	4.5	5.1	7.8	3.9	"	"	"	"	3.0	2.1
10th	2.1	2.7	3.9	9.8	7.8	6.3	"	"	"	"	3.0	1.8
11th	1.2	2.7	2.7	8.4	6.3	7.5	"	"	4.2	"	2.4	1.8
12th	1.5	3.0	3.6	6.3	7.5	rainy day	3.9	"	3.3	"	3.0	1.5
13th	1.5	2.4	rainy day	6.6	7.5	"	3.6	"	rainy day	3.9	...	1.5
14th	1.3	2.1	"	5.7	7.8	3.3	rainy day	"	"	5.1	...	1.2
15th	1.6	2.1	4.8	5.1	7.8	3.3	"	"	"	5.1	...	2.1
16th	1.2	2.4	5.7	6.3	7.2	3.0	"	"	"	4.5	...	1.8
17th	3.0	2.1	5.7	5.7	6.9	3.3	"	"	3.0	3.6	...	1.8
18th	1.8	2.7	3.0	5.4	7.2	rainy day	"	"	rainy day	4.5	...	1.8
19th	1.5	2.4	3.6	9.2	6.6	"	"	"	"	4.2	...	2.1
20th	2.7	3.6	rainy day	rainy day	10.1	"	4.2	6	"	3.6	...	2.1
21st	2.4	2.7	6.6	"	7.8	"	4.8	rainy day	"	3.0	...	1.8
22nd	1.5	3.0	8.7	4.5	8.1	"	5.1	"	2.7	3.3	...	2.1
23rd	2.1	1.8	5.7	4.2	6.9	"	rainy day	"	3.6	3.0	...	2.1
24th	1.8	2.1	4.2	4.8	rainy day	"	3.6	"	rainy day	3.0	1.8	1.8
25th	2.7	2.7	3.9	4.8	"	"	4.8	"	"	3.0	1.5	2.1
26th	1.5	3.3	3.9	4.8	5.4	"	3.6	3.6	rainy day	3.0	1.5	1.5
27th	rainy day	3.3	rainy day	4.5	6.9	1.5	rainy day	3.0	2.4	2.7	3.0	1.5
28th	3.9	2.7	3.3	7.2	rainy day	3.3	4.2	rainy day	2.7	3.0	2.4	1.5
29th	5.4	...	3.3	9.8	5.4	3.9	4.5	"	2.4	3.3	2.4	1.5
30th	2.7	...	3.6	11.0	6.3	4.2	3.6	"	rainy day	3.0	2.7	1.5
31st	2.7	...	3.3	...	4.8	...	rainy day	"	...	3.0	...	1.5

## J. WALTER LEATHER.

STATEMENT I—(continued).  
*Evaporation from a plain water surface at the Agricultural Research Institute, Pusa (1912).*

[Date.]	January.	February.	March.	April.	May.	June.	July.	August.	September.	October.	November.	Dec.
1st	mm. 1.8	mm. 1.2	mm. 3.9	mm. 3.6	mm. 5.4	mm. 6.0	mm. rainy day	mm. rainy day	mm. 3.0	mm. rainy day	mm. rainy day	mm. 2.7
2nd	1.5	rainy day	3.9	3.6	6.0	rainy day	"	"	"	"	"	2.7
3rd	1.8	1.8	3.0	2.7	6.9	3.9	"	6.0	"	3.6	2.4	2.1
4th	1.5	2.7	3.6	3.6	6.3	rainy day	"	rainy day	"	3.6	2.1	1.8
5th	1.5	2.7	4.5	4.8	6.3	5.4	"	4.5	"	4.2	2.7	1.8
6th	1.5	2.7	4.2	7.2	5.7	rainy day	3.6	4.8	"	4.2	2.7	1.8
7th	1.5	2.1	3.9	7.2	5.7	rainy day	rainy day	rainy day	"	3.9	3.0	1.8
8th	1.5	2.4	3.3	6.6	7.2	6.0	rainy day	"	"	3.9	3.0	1.8
9th	1.8	1.5	3.6	5.7	6.0	rainy day	3.9	"	"	3.9	3.0	1.8
10th	1.5	1.8	3.9	5.1	6.0	4.8	rainy day	"	2.1	3.3	2.4	2.1
11th	rainy day	2.4	4.2	6.3	6.9	4.8	"	"	4.2	3.6	3.0	2.4
12th	1.5	2.7	4.8	4.8	6.6	4.8	"	"	4.5	4.5	3.0	2.1
13th	9	2.7	4.5	3.9	5.7	4.8	"	"	4.5	3.9	2.7	1.8
14th	1.5	2.7	5.7	4.8	7.2	5.4	"	2.4	3.9	3.6	3.0	1.8
15th	1.5	2.4	7.5	5.1	rainy day	6.0	1.8	rainy day	3.9	4.5	3.3	2.4
16th	1.8	2.4	5.4	4.5	4.5	6.3	3.9	"	3.9	6.0	3.0	1.8
17th	1.5	2.7	5.1	rainy day	4.8	6.9	3.9	"	3.6	5.1	3.3	2.1
18th	2.1	2.4	4.5	4.2	4.2	7.2	rainy day	"	3.6	3.6	2.7	1.2
19th	1.5	2.7	3.0	4.2	4.5	7.5	rainy day	"	4.2	3.6	3.0	1.2
20th	1.8	2.7	5.4	rainy day	4.8	6.6	rainy day	"	5.1	3.6	2.4	1.8
21st	1.8	2.7	6.9	5.1	rainy day	6.0	3.3	2.1	5.1	3.6	2.7	1.8
22nd	1.8	2.7	4.2	4.8	6.0	rainy day	2.1	rainy day	4.8	3.9	rainy day	2.1
23rd	1.5	2.7	3.6	3.6	6.0	rainy day	2.4	rainy day	3.9	4.2	"	1.8
24th	1.8	2.7	3.9	3.0	6.9	5.1	3.0	3.3	3.3	3.9	1.8	1.5
25th	1.8	2.1	3.0	5.4	5.7	rainy day	rainy day	rainy day	3.3	3.6	2.4	1.5
26th	2.1	4.5	3.3	5.4	5.7	"	3.6	3.9	3.3	3.6	2.4	1.8
27th	2.4	4.2	rainy day	5.1	5.7	rainy day	rainy day	rainy day	4.2	3.6	2.1	1.8
28th	1.8	3.9	4.2	5.4	6.6	4.5	rainy day	4.2	3.9	3.0	2.1	1.8
29th	1.8	3.3	rainy day	6.0	6.0	rainy day	5.7	rainy day	3.6	3.3	2.4	1.8
30th	1.2	...	rainy day	6.0	6.3	...	4.8	rainy day	3.9	3.9	...	1.8
31st	1.2	...	3.9	...	6.3	...	4.8	3.9	...	3.9	...	1.8





## STATEMENT II.

*Observed rates of evaporation in mm. per 24 hours.*

Month.	Pusa, 1911.	Pusa, 1912.	Lyallpur, average of 4 years.	Madras, average of 5 years.
January ...	1.86	1.64	1.83	3.91
February ...	2.58	2.61	2.64	4.67
March ...	4.04	4.30	4.10	5.23
April ...	6.00	4.90	5.78	6.32
May ...	6.87	5.94	9.88	6.91
June ...	4.46	5.80	9.37	7.44
July ...	4.22	3.90	7.76	6.20
August ...	3.37	3.72	6.95	5.89
September ...	3.10	3.95	6.15	4.52
October ...	3.42	3.93	4.90	4.49
November ...	2.95	2.68	3.00	4.01
December ...	1.86	1.91	1.98	3.86

Owing to the circumstance already explained, the evaporation at Pusa is only known for dry days, and hence the total annual evaporation can only be estimated by the aid of the formula which is subsequently discussed. In order to calculate, at least approximately, the total evaporation at Pusa, it has been assumed for wet days, that this is nominal for days on which more than .5" of rain fell, whereas on the remaining wet days the quantity is that which may be calculated by my formula from the meteorological data. The total annual evaporation at Pusa in comparison with Lyallpur and Madras may then be thus compared (centimeters).

	Pusa.				Lyallpur.	Madras.
	No. of days.	1911.	No. of days.	1912.		
Observed dry days ...	280	104.5	303	111.8		
Calculated for wet days ...	59	20.9	39	14.6		
TOTAL ...		125.4		126.4	196.2	193.2
		4.12ft.		4.18ft.	6.42 ft.	6.34 ft.

The similarity of the amounts of evaporated water at Lyallpur and at Madras respectively is naturally merely accidental.

*The calculation of evaporation from a plain water surface.*—Many attempts have been made and much time has been spent in the evolution of a mathematical formula which will express

the amount of water which evaporates from a plain water surface. Thus we have:—

1. Russell's

$$E = \frac{\text{inches}}{\text{month}} = \frac{30}{B} [43.88 (e_i - e_d) + 1.96 e_i]$$

in which, E = evaporation

$e_i$  = vapour pressure at temperature of wet bulb thermometer

$e_d$  = vapour pressure at dew point temperature.

2. Abbassia's

$$E = \frac{\text{mm.}}{\text{hour}} = .0122 (e_w - e_d) + .00029 (e_w - e_d)v$$

3. Fitzgerald's

$$E = \frac{\text{mm.}}{\text{hour}} = .0166 (e_w - e_d) + .000783 (e_w - e_d)v$$

4. Carpenter's

$$E = \frac{\text{mm.}}{\text{hour}} = .0161 (e_w - e_d) + .0000895 (e_w - e_d)v$$

5. Stelling's

$$E = \frac{\text{mm.}}{\text{hour}} = .0351 (e_w - e_d) + .00044 (e_w - e_d)v$$

where in the last four of which,

$e_w$  = vapour pressure at the water surface temperature

$e_d$  = vapour pressure at the dew point temperature

$v$  = wind velocity in metres per second.

F. H. Bigelow\* in an article compares these formulæ under stated circumstances and since they yield very widely different results, he concludes that none is reliable. Another formula of Russell's is:— $A p_w + B (p_w - p_a)$

in which  $p_w$  = vapour tension corresponding to the wet bulb thermometer

$p_a$  = vapour tension corresponding to the dew point.

$$A = 1.96$$

$$B = 43.9$$

This formula also seems to yield very incorrect results; that in one quoted example being only two-thirds of the directly ascertained quantity.

\* U. S. A. Monthly Weather Review, July 1907.

In any case each of these formulæ depends on the possession of correct information regarding the aqueous tension of the atmosphere as well as generally the wind velocity. But there is nothing more difficult to obtain than a continuous record of vapour tension and it is very much simpler to determine the evaporation directly. In fact, a formula to be of any practical utility must depend simply on the usual meteorological data of the country, namely, mean temperature, humidity and wind velocity.

After plotting the results of evaporation at Pusa as shown in Charts I & II an attempt was made to derive an empirical formula which might meet the case. It was assumed that a formula of the type  $E = t^x D^y W^z$  would satisfy the conditions in which

- $E$  = evaporation ;
- $t$  = the temperature of the atmosphere ;
- $D$  = the dryness of the atmosphere ;
- $W$  = the wind velocity.

Regarding  $D$ , it is the difference between 100 per cent. and the relative humidity. It seemed probable that if, instead of relative humidity, the difference between 100 per cent. and this figure were used, the effect of this factor would be more pronounced. For example, there is a greater relative difference between 20 per cent. and 10 per cent. of "dryness" than between 80 per cent. and 90 per cent. humidity.

For the end in view the mean data of short periods during December, March and April—about six days each—when the atmospheric conditions were very uniform, were set out. The values of the indices  $x$ ,  $y$ ,  $z$  were then obtained by the method of least squares, which yielded:—

$$x = -\cdot11786$$

$$y = +\cdot44366$$

$$z = +\cdot215994$$

$$E = \text{mm. per 24 hours.}$$

This equation then yielded values of evaporation for Pusa which agree well with the evaporimeter record. But on applying it to

Punjab data, it proved highly defective. Moreover, the negative value of  $x$  rendered it from the first unlikely to be generally useful.

Another formula which seems to be more generally useful was obtained by (a) plotting the logs of the three factors, temperature, dryness and wind velocity, against the log of evaporation, from which values of the type

$$a (\log t - b)$$

were obtained, which proved a suitable basis to work from, and then (b) by a series of approximations the following more accurate values were obtained :—

$$E = (\text{mm. per 24 hrs.}) = 2.0 (\log t - 1.74) \\ + .33 (\log D - 1.00) + .36 (\log W - .125)$$

in which

$t$  = mean temperature °F. for day ;

$D$  =  $100 - 8$  A.M. humidity ;

$W$  = mean wind velocity for day ;

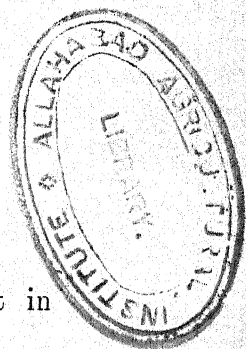
common logs were naturally employed.

This formula has yielded the results which are set out in Statements Nos. III, IV & V.

It will be seen that for the majority of months the calculated evaporation agrees fairly well with the actual ; there are 14 cases among the 48 in which the divergence exceeds about 10 per cent. and 5 cases in which it exceeds 20 per cent. Some of these cancel one another during the year. Thus the following shows the annual evaporation, in *centimetres* at the three stations :—

		Actual cm.	Calculated cm.	Error.
Pusa 1911	...	* 104.5	99.7	5%
Pusa 1912	...	* 111.8	109.1	2%
Lyalpur	...	196.2	194.8	6%
Madras	...	193.2	179.5	7%

\* Dry days only.





Hence for the approximate estimation of the annual evaporation from the ordinary meteorological data the formula may be relied upon. On the other hand, the error which may occur in individual estimates may be serious.

Although my formula is a purely empirical one, it is apparently a considerable advance on any of those previously used. At the same time there is no doubt that for an accurate record of evaporation it is much better to ascertain this directly than to rely on the formula, and it is also simpler to do so than to estimate specially the several meteorological factors.

## STATEMENT III.

*Evaporation from a plain water surface at PUSA as experimentally determined, and calculated from meteorological data respectively.*

MONTH.	Mean temperature °F.	Mean humidity 8 A.M.	Dryness.	Mean wind velocity miles per hour.	EVAPORATION.	
					Found mm. per 24 hours.	Calculated mm. per 24 hours.
1911						
January	62.7	90.6	9.4	3.20	1.86	1.75
February	64.1	78.75	21.25	2.78	2.58	2.28
March	72.5	62.24	37.76	4.32	4.04	4.14
April	83.8	57.0	43.0	4.83	6.00	6.01
May	87.9	69.25	30.75	6.99	6.87	6.75
June	88.0	70.0	30.0	4.74	4.46	5.84
July	86.7	82.3	17.7	4.23	4.22	4.56
August	85.1	89.2	10.8	2.75	3.37	3.19
September	84.4	85.5	14.5	3.05	3.10	3.60
October	78.8	85.1	14.9	1.84	3.42	2.64
November	69.1	86.5	13.5	1.74	2.95	1.94
December	60.7	91.9	8.1	2.24	1.86	1.34
1912						
January	61.7	92.3	7.7	2.89	1.64	1.53
February	67.0	82.5	17.5	2.97	2.61	2.39
March	73.4	57.7	42.3	4.90	4.30	4.61
April	80.4	66.7	33.3	5.60	4.90	5.12
May	86.9	69.3	30.7	5.36	5.94	6.00
June	88.6	76.1	23.9	5.04	5.80	5.61
July	85.5	85.9	14.1	6.02	3.90	4.67
August	85.0	84.5	15.5	4.48	3.72	4.28
September	84.1	78.5	21.5	2.80	3.95	3.95
October	79.3	75.7	24.3	1.74	3.93	3.08
November	69.1	82.2	17.8	2.42	2.68	2.37
December	61.8	89.8	10.2	1.96	1.91	1.46

NOTE.—These data refer to dry days only.

## STATEMENT IV.

*Evaporation from plain water surface at Lyallpur as experimentally determined and calculated from meteorological data respectively.*

MONTH.	Mean temperature °F.	Mean humidity 8 A.M.	Dryness.	Mean wind velocity miles per hour.	EVAPORATION.		
					Found.		Calculated.
					ft. per hour.	mm. per 24 hours.	mm. per 24 hours.
January...	54	75	25	2.5	.00025	1.83	1.76
February...	59	70	30	3.5	.00036	2.64	2.35
March ..	70.5	60	40	6.0	.00056	4.10	4.49
April ...	81	45	55	4.0	.00079	5.78	5.70
May ...	91	40	60	6.0	.00135	9.88	8.56
June ...	96	47	53	6.0	.00128	9.37	9.14
July ...	92.5	75	25	6.0	.00106	7.76	6.61
August ...	90	70	30	5.0	.00095	6.95	6.83
September...	87	60	40	5.0	.00084	6.15	6.40
October...	78	50	50	2.0	.00067	4.90	3.99
November...	66	55	45	2.5	.00041	3.00	2.99
December...	56	65	35	2.0	.00027	1.98	1.82

NOTE.—The meteorological data for Lyallpur were taken from Elliot's meteorological atlas. The record of evaporation is that published by the Public Works Department, Irrigation Branch, and is an average of 4 years, 1906-1910.

## STATEMENT V.

*Evaporation from plain water surface at Madras as experimentally determined and calculated from meteorological data respectively.*

MONTH.	Mean temperature °F.	Mean humidity 8 A.M.	Dryness.	Mean wind velocity miles per hour.	EVAPORATION.		
					Found.		Calculated.
					Inches per 24 hours.	mm. per 24 hours.	mm. per 24 hours.
January...	74.6	82.6	17.4	4.48	.154	3.91	3.48
February...	78.9	92.0	8.0	3.69	.134	4.67	2.76
March ...	83.0	78.1	21.9	5.74	.206	5.23	5.01
April ...	85.1	74.3	25.7	4.97	.249	6.32	5.27
May ...	91.4	64.6	35.4	6.32	.272	6.91	7.38
June ...	92.4	62.7	37.3	6.53	.293	7.44	7.77
July ...	88.3	68.8	31.2	4.87	.244	6.20	6.01
August ...	86.9	75.3	24.7	4.55	.232	5.89	5.26
September...	86.5	77.7	22.3	3.93	.178	4.52	4.65
October...	83.0	82.7	17.3	3.45	.177	4.49	3.86
November...	78.9	83.3	16.7	4.33	.158	4.01	3.74
December...	75.8	82.8	17.2	5.00	.152	3.86	3.67

NOTE.—The meteorological data for Madras are taken from the India Daily Weather Report. The record of evaporation is the average of 5 years' records, 1898 to 1903, which were communicated by the Meteorological Department.





STUDIES IN THE CHEMISTRY AND PHYSIOLOGY  
OF THE LEAVES OF THE BETEL-VINE (*PIPER  
BETLE*), AND OF THE COMMERCIAL BLEACH-  
ING OF BETEL-VINE LEAVES.

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THE use of the leaves of the betel-vine as a material for chewing is one of the peculiar practices of South Eastern Asia and especially of India, but in these countries it is nearly universal. Hence the plant is grown in almost every province of India, and grown under very special and peculiar conditions. The betel-vine, as is well known, is a creeper, grown always in intense shade,—the leaves being injured by exposure even for a short time to the sun,—with a continually moist atmosphere. These necessary conditions indicate that it must be, as it is, a very intensive cultivation, calling for the laying out of large capital to establish a 'pan' (or betel-vine) garden, but one which yields, if successful, very large returns. The actual condi-

tions of cultivation have been often described,\* and there is no need to repeat the description here.

It might have been anticipated that a product grown on such a large scale, and forming such a common article of consumption in India would have been the frequent subject of chemical investigation. This has, however, not been the case and with the exception of chemical enquiries made in Java, in Germany, and also in Western India† into the nature of the essential oil, very little has been done to elucidate the nature of the leaf or the causes which make it so highly valued. We have had the opportunity of investigating certain aspects of the chemistry and physiology of the leaves and betel-vine plants, and propose to consider the results which we have obtained up to date under the following heads :—

- I. The occurrence of nitrates in betel-vine leaves, and plants, and their relationship to the growth of their vine.
- II. The sugars, starch, tannin, essential oil and other normal constituents of the betel-vine and their relationship to the growth of the vine.
- III. The commercial bleaching of the betel-vine leaf, and the chemical changes by which it is accompanied.

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\* *Vide* Watt's Dictionary of the Economic Products of India, Article *Piper betle*. Also Agricultural Journal of India, Vol. IV, pp. 365—374; and Poona Agricultural College Magazine, Vol. II, No. 2 : Vol. IV, No. 1.

† Kemp, quoted by Dymock, Warden & Hooper. *Pharmacographica Indica*. Part III, p. 188.

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## I.

THE OCCURRENCE OF NITRATES IN BETEL-VINE LEAVES AND PLANTS,  
AND THEIR RELATIONSHIP TO THE GROWTH OF THE VINE.

THE occurrence of fairly large quantities of nitrates in the growing leaves of plants has hardly been known hitherto, and in the present case it was totally unsuspected. Our investigations simply, in fact, commenced with an attempt to ascertain the constituents, chiefly organic, which occur in the leaves and which are likely to play some part in the attractiveness of the leaves to an Indian palate.

A large quantity of *pan* (betel-vine) leaves, as they are bought in the bazar, was dried in the sun for two days, when they could be coarsely powdered by rubbing with the hands. This material was then successively extracted with Petroleum Ether (B.P. 35°-58° C.), Ether, Chloroform, Acetic Ether, and Alcohol. The percentages of the dry leaf extracted by these solvents were as follows :—

Solvent.	Extract. Per cent.
Petroleum Ether	3.33
Ether	1.16
Chloroform	1.27
Acetic Ether	.76
Alcohol	6.61
	13.13

Sixteen hundred grammes of the dried leaves were then extracted by continuous percolation with hot alcohol, the temperature being maintained constant at 65°C. by a water jacket. The extraction was continuous until the extract, at first dark green in colour, became colourless. This required about ten litres of alcohol.

On standing, this extract deposited a considerable quantity of crystals on the sides and bottom of the vessels in which the percolated liquid was received. The whole of the liquid was, therefore,



filtered, the crystals extracted with water, in which they proved to be soluble, and recrystallised. The amount thus obtained weighed 4.41 grammes or 0.26 per cent. of the original dried leaves.

Much to our surprise this crystalline substance obtained directly by the extraction of betel-vine leaves with alcohol, proved to be nothing else than Potassium Nitrate. By concentration of the filtrate from the first crop of crystals, and extraction of the residue with water, the actual amount of Potassium Nitrate obtained reached 11.9 grammes or 0.74 per cent. of the original dried leaves.

This was a totally unexpected result. Nitrates occur in minute quantities in many plant tissues, but there are hardly any cases where they exist in a proportion greater than 0.1 per cent. of the dried tissue, and it seemed important to ascertain how far the occurrence was a constant one.

Nitrates were therefore determined by direct estimation in the leaves by Schloesing's method. In order to do this it was only necessary to prepare a water extract of the leaves, and heat this, in the usual manner, in a current of carbon dioxide with ferrous chloride and sulphuric acid. The volume of nitric oxide evolved gives a direct measure of the amount of nitrate and nitrite present. This has been done in a large number of cases with leaves taken from various parts of the betel-vine. In the first series of determinations, three leaves were taken, on branches of the vine, from those nearest the main stem of the vine and from those which were furthest away. The results are shown in the table.

Date 1911.	Position of Leaves on Branch.	Dry matter.	Potassium Nitrate in Fresh Leaves.	Potassium Nitrate in Dry Leaves.
		Per cent.	Per cent.	Per cent.
May 22nd	.....	.....	.36	.....
June 10th	Leaves furthest from vine	14.4	.37	2.62
June 10th	Leaves nearest vine	16.0	.42	2.66
June 17th	Leaves furthest from vine	12.8	.26	2.38
July 8th	Leaves furthest from vine	12.8	.32	2.50
July 8th	Leaves nearest vine	14.0	.36	2.56
July 22nd	Leaves furthest from vine	12.8	.30	2.32
July 22nd	Leaves nearest vine	14.4	.35	2.49

This table shows that the actual quantity of Potassium Nitrate in the leaves is higher than was apparent from our original extracts. Calculated from the nitric acid found by Schloesing's method on the fresh leaf the percentage naturally varies with the amount of moisture present in the leaves at that particular time,—but calculated on the dry matter, the amount seems fairly constant, and varies between 2·3 and 2·7 per cent. of the dry leaf.

The existence of this nitrate constantly in the leaves of the betel-vine at once raised the question as to what purpose it could serve, and the first steps to ascertain this could only be taken by ascertaining its distribution in the plant. With this object, determinations of nitrate were made, by Schloesing's method, from material taken from different parts of the vine plants.

1.—*Comparison of the branches and the leaves growing on them.*

No.	Branches. Potassium Nitrate in dry matter.	Leaves growing on the Branches. Potassium Nitrate in dry matter.
	Per cent.	Per cent.
1	2·55	2·01
2	2·13	1·74

These figures would indicate that the branches contain more nitrate than the leaves by about twenty-five per cent.

2.—*Comparison of the various leaves from the main vine stem.*

This comparison, as the following figures indicate, shows that the young tender leaves of the tips of the main vine contain a very small quantity of Nitrate, but as one proceeds further down the vine the percentage increases. Ten vines of nearly the same height were selected and the leaves growing on the main stem were sorted. The topmost four leaves were placed together for analysis, the next four together, and so on to the seventeenth leaf.



No.	Leaves.	Potassium Nitrate on dry leaf.
1	Topmost four leaves ... ..	Per cent. 0.63
2	5th to 8th leaf from top ... ..	1.50
3	9th to 12th leaf from top ... ..	1.50
4	13th to 17th leaf from top ... ..	2.05

The leaves on the main vine are not much used for chewing.

3.—*Comparison of various branches, and of the leaves from these branches.*

Ten whole vines except the lowermost two feet were taken and divided into different parts. The two pairs of branches nearest the tip were placed together: then the third pair of branches: then the fourth and so on. In each case the leaves on these branches were examined for nitrate separately from the branches themselves. The following table shows the results:—

No.	Number of Branch (Counting from top.)	Leaves on Branch, Potassium Nitrate on dry matter.	Branches, Potassium Nitrate on dry matter.
		Per cent.	Per cent.
1	1st and 2nd branches ... ..	1.66	2.92
2	3rd branch ... ..	1.93	3.76
3	4th do. ... ..	2.13	3.74
4	5th do. ... ..	2.43	3.82
5	6th do. ... ..	2.22	3.76
6	7th do. ... ..	2.10	3.90
7	8th do. ... ..	2.31	3.93
8	9th do. ... ..	2.01	3.97
9	10th do. ... ..	2.50	3.26

This table shows clearly that the youngest leaves and branches do not contain so much nitrate as those which are more mature. Among the mature leaves and branches there is not much change in the quantity, but the branches (stems) always contain very much more nitrate than the leaves themselves.

4.—*Comparison between various portions of the main vines.*

The portions of the vine were taken so that the stem between each pair of branches formed a sample. Thus the topmost portion of the stem to the origin of the second pair of branches

formed one sample, that between the second and third pair formed a second, that between the third and the fourth a third and so on. The results of analysis are indicated in the following table :—

No.	Position of Vine.	Potassium Nitrate on dry leaf.
		Per cent.
1	Vine above the 2nd branches ... ..	4.46
2	Do. between 2nd & 3rd „ ... ..	3.05
3	Do. do. 3rd & 4th „ ... ..	2.04
4	Do. do. 4th & 5th „ ... ..	2.00
5	Do. do. 5th & 6th „ ... ..	2.19
6	Do. do. 6th & 7th „ ... ..	2.01
7	Do. do. 7th & 8th „ ... ..	1.50
8	Do. do. 8th & 9th „ ... ..	1.33
9	Do. do. 9th & 10th „ ... ..	0.98
10	Do. below 10th „ ... ..	0.72

These results are extremely curious. The younger stem contains far more nitrate than the lower portions, while (*vide comparison 2*) the leaves growing from these younger stems contain very little. To confirm the results, repetition of the examination of leaves from various parts of the main vine was undertaken.

5.—*Comparison of the various leaves from the main vine stem.  
(Repetition of comparison No. 2).*

No.	Leaves.	Potassium Nitrate (on dry leaf.)
1	Topmost four leaves ... ..	.68
2	5th to 8th leaf from top ... ..	1.66
3	9th to 12th leaf from top ... ..	1.94
4	13th to 16th leaf from top ... ..	2.01
5	17th to 20th leaf from top ... ..	2.04
6	21st to 24th leaf from top ... ..	2.18
7	25th to 28th leaf from top ... ..	2.17

These figures confirm in every particular the former comparison.

The results brought out in these tables may be summarised as follows :—

- (1) All parts of the living betel-vine plant contain nitrates.
- (2) In the main stem, the amount of nitrate increases towards the growing tip.

(3) In the leaves on the main stem, on the contrary, the younger leaves contain by far the least amount of nitrate. As the leaves mature, they, however, very rapidly reach what may be called a normal amount.

(4) The youngest branches and the leaves growing thereon contain less nitrates than the mature ones. There is little difference between the various leaves and the various branches which have become mature.

(5) In general, the stems contain more nitrate than the leaves.

What then is the position of nitrate in the economy of the betel-vine plant? Of course, at the present stage it is impossible to do more than to put forward a few tentative suggestions, but it seems worth while to try and do this. In the first place it would seem that the nitrate in this case is absorbed direct from the root. Whether it is absorbed by the root, and transmitted without change, we do not know: on this point our figures give us no information. But it passes up the stems, and tends to concentrate in the upper part of the main stem. In the young and growing leaves and branches however, very rapid reduction of the nitrate takes place, and the quantity remaining is very small. The mature leaves seem to have very much less effect in reducing nitrates, though they have some. But the rapid reduction of the nitrates in the leaves and stems seems to be coincident with very active growth, such as occurs in young structures only. It might be hazarded that here we have, possibly, direct supply of nitrogen for growth to the leaves and shoots in the form of nitrates, and that in this case the reduction of the nitrate is done by the growing structure itself, instead of, as is usual, by the root of the plant. This is at any rate the direction to which our results lead, but a good deal more work will be required before this can be stated with confidence.

## II.

THE SUGAR, STARCH, TANNIN AND ESSENTIAL OIL AND OTHER  
NORMAL CONSTITUENTS OF THE BETEL-VINE AND THEIR  
RELATIONSHIP TO THE GROWTH OF THE VINE.

THE original question which led to the present investigation was as to what is the cause of the use of the betel-vine leaf for chewing purposes. It was quickly found that no appreciable quantity of an alkaloid was present in the leaf, and no active glucoside seemed to be present. To what extent, then, are the other constituents normal, and to what extent do they differ in quantity in the various parts of the betel-vine plant. This was the question which we placed before ourselves, and we resolved to investigate the following normal constituents: (1) the tannin; (2) the sugars; (3) the starch; (4) the ether extract; (5) the essential oil; (6) the acidity; and (7) the diastatic activity. Put in this form, the inquiry has not proceeded very far, but the results we have obtained are at least suggestive.

The methods of estimation of these various constituents were as follows:—

(1) The sugars (reducing and non-reducing), and starch were determined almost exactly by the methods described by Brown and Morris in their account of their investigation of foliage leaves in 1893. In this the leaves are dried in an oven after placing them for a few minutes in chloroform vapour, or dipping them in alcohol—the latter by preference. The dried leaves are thoroughly powdered and extracted with ether to remove chlorophyll and fats. A definite weight is then taken for the starch determination (10 grammes). This quantity is placed in a flask and digested with alcohol of about 80 per cent. strength for 24 hours at 40° C. The alcohol is then poured off, and the extraction repeated. After the second extraction, the residue is repeatedly washed by decantation with warm alcohol, until the washings are free from colour. The residue from the alcohol treatment after drying is mixed with a little warm water, and



the mixture heated in a bath of boiling water to complete the gelatinisation of the starch. It is then cooled to 50° C., and malt extract is added (in which the sugar has been separately determined) and the conversion of the starch done for two hours at 50-55° C. The mixture is then raised to the boiling point, the solid matter removed by filtration and the cupric reducing power of the filtrate determined in the usual manner.

The original alcohol extract of the leaves, containing the sugars, is evaporated to dryness, after addition of a drop or two of ammonia to prevent possible inversion. The residue after addition of water is poured into a 100 cc. flask, 1 cc. of a strong solution of basic lead acetate added, and the whole made up to 100 cc. Basic lead acetate removes tannin and other matters which may interfere with sugar determination. The filtrate from the precipitate produced by the basic lead acetate is treated with sulphuretted hydrogen, filtered and washed, and then evaporated to remove sulphuretted hydrogen. The liquid contains the sugars from the original ten grammes of leaves. The reducing sugars are determined in the solution by Fehling's method volumetrically. The remaining solution is then treated with hydrochloric acid and kept on the water bath. After this the reducing power is again determined by Fehling's solution, and this gives a measure of the non-reducing sugars.

(2) The ether extract was determined by extracting the leaf dried *in vacuo* in a Soxhlet extractor in the usual way.

(3) The essential oil was determined by taking ten grammes of fresh leaves and distilling with steam from a separate vessel. The distillate obtained was shaken with ether five to six times. The ether extract was evaporated at the ordinary temperature, and the residue dried in a vacuum desiccator, and weights taken until it becomes constant.

(4) The tannin. Two grammes of dried leaves or eight to ten grammes of fresh leaves were extracted three times for half to one hour with one hundred cubic centimeters of boiling water. The extract was filtered hot each time. The various portions of the filtrate were brought to the boil and the tannin precipitated by



the addition of twenty to thirty cubic centimeters of copper acetate solution. The precipitate was filtered and the filtrate always appeared green with the excess of copper acetate. The precipitate was washed, dried and burnt in a porcelain crucible. After cooling a little nitric acid is added and all the copper converted into cupric oxide by heating. The residue is copper oxide and one gramme of this is taken as equivalent of 1.306 grammes of tannin.

(5) In estimating the acidity one hundred grammes of the fresh leaves were taken, and soaked in 500 cc. of cold water for twenty hours. The acidity of the liquid was then determined by decinormal solution of caustic potash, using phenol phthalein as indicator.

(6) The diastatic activity was estimated precisely by the method devised by Brown and Morris in 1893 (*loc. cit.*). This is as follows :—Half a gramme of the finely powdered air dried leaf was digested at 30° C. with 50 cc. of a 2 per cent. solution of soluble starch which had been previously prepared by the limited action of hydrochloric acid on starch according to the method of Lintner. The digestion of the mixture was carried on for exactly forty-eight hours, the danger of any appearance of micro-organisms being averted by employing chloroform at the rate 5 cc. per litre of starch solution. A duplicate experiment was made by taking the same amount of leaf and starch solution, boiling the mixture for a minute or two and placing alongside the first solution. This solution was used for correcting the first solution for cupric reducing power of the sugars naturally contained in the leaf.

The difference between the cupric reducing powers of the first and second solutions was a measure of the hydrolytic work done and it became possible when the time and all other conditions remain constant to compare the relative diastatic activities in this way.

The cupric reduction was calculated in all cases as maltose and for purposes of comparison this was referred to one hundred grammes of the dry leaf so that the numbers indicating the relative diastatic activity really represent the number of grammes of maltose which the diastase of one hundred grammes of leaf is

able to produce from soluble starch by hydrolysis in forty-eight hours at a temperature of 30°C.

A number of betel-vine plants were taken and stripped of leaves at the same time, the leaves being divided into several lots, as follows :—

*Leaves from the main vine—*

- (1) Leaves from the topmost two feet of the main vine.
- (2) Leaves from two to four feet from the top of the main vine.
- (3) Leaves from four to six feet from the top of the main vine.

*Leaves from the branches—*

- (1) Leaves from all branches whose origin is within two feet of the top of the vine.
- (2) Leaves from all branches whose origin is from two to four feet from the top of the vine.
- (3) Leaves from all branches whose origin is from four to six feet from the top of the vine.

The vines used were not completely grown, their height being on the average, about nine feet. There are seldom any branches or leaves within three feet of the ground, and so the analyses made included practically leaves from all parts of the vine.

All the samples were taken at one time in the morning (10 A.M.).

The results are indicated in the following series of tables. All percentages (except where otherwise indicated) are on the dry leaves :—

1. *Sugars—*

	Reducing sugars (as glucose).	Non-reducing sugars (as saccharose).	Total sugars.
	Per cent.	Per cent.	Per cent.
I. Leaves from the main vine—			
(1) Within two feet of tip ...	1.60	1.20	2.80
(2) 2 to 4 feet from tip ...	1.41	1.31	2.72
(3) 4 to 6 feet from tip ...	1.55	1.18	2.73
II. Leaves from branches—			
(1) Within 2 feet of tip of main vine ...	3.17	2.48	5.65
(2) 2 to 4 feet from tip of main vine ...	2.26	1.12	3.38
(3) 4 to 6 feet from tip of main vine ...	1.86	.59	2.45

So far as the leaves on the main vine are concerned, the amount of both reducing and non-reducing sugars is very constant. But when the results from the branches are taken, there is a very marked difference. On the whole, the total amount of sugars in the leaves on the branches is higher than in those on the main stem, except with regard to the branches on the lower part of the vine, where the non-reducing sugars are very low indeed. But among the branches themselves, there is a very large difference. The upper branches that is to say the younger branches bear leaves with a very large sugar content, both reducing and non-reducing. This amount declines regularly as one proceeds lower and lower in the branches originating lower and lower in the creeper. The decline is proportionately greater in the non-reducing sugars than in the reducing sugars as the following figures indicate :—

	Reducing sugars.	Non-reducing sugars.
	Per cent.	Per cent.
1. Leaves on middle branches contain less than those on the topmost branches by ... ..	28.7	54.8
2. Leaves on lower branches contain less than those on the topmost branches by ... ..	41.3	76.2

The meaning of this can best be discussed, perhaps, in connection with the figures for the percentage of starch.

2. *Starch*—

				Starch.
				Per cent.
I. Leaves from the main vine—				
1.	Within two feet of tip	...	...	1.1
2.	2 to 4 feet from tip	...	...	1.1
3.	4 to 6 feet from tip	...	...	1.0
II. Leaves from branches—				
1.	Within two feet of tip of main vine	...	...	1.2
2.	2 to 4 feet from tip of main vine	...	...	1.2
3.	4 to 6 feet from tip of main vine	...	...	1.2

Here we have an extraordinary constancy. The amount of starch hardly varies at all between the leaves in the main vine,

and those on the branches,—and also between the leaves on the upper and lower parts of the vine,—when, it is understood, the leaves are collected in the morning.

If we take these figures with those which have already been given for the sugars, they would simply seem to indicate that the physiological processes of metabolism are much more active in the younger leaves near the top of the plant than in the lower part. In both cases the starch is small in amount, as would be expected in the morning. The relationship between the reducing and non-reducing sugars in leaves from branches in different parts of the vine seems significant of much more than this. On the branches from the upper part of the plants the non-reducing sugars in the leaves are 78·2 per cent. of the reducing sugars: on the middle branches the non-reducing sugars in the leaves are 49·8 per cent. only of the reducing sugars: on the lower branches, the non-reducing sugars are 31·7 per cent. only of the reducing sugars. In other words where absorption and metabolism are most vigorous, in the early morning the non-reducing sugars are very large in proportion to the reducing sugars. This would seem to be, on the whole, evidence that non-reducing sugar (say saccharose) is a first product of carbon dioxide absorption.

3. *Ether Extract*— }  
4. *Essential Oil*— }

						Ether Extract.	Essential Oil.
						Per cent.	Per cent.
I. Leaves from the main vine—							
1.	Within two feet of tip	...	...	...	...	8·0	1·6
2.	2 to 4 feet from tip	...	...	...	...	8·5	1·2
3.	4 to 6 feet from tip	...	...	...	...	8·1	1·1
II. Leaves from the branches—							
1.	Within 2 feet of tip of main vine	...	...	...	...	7·5	1·8
2.	2 to 4 feet from tip of main vine	...	...	...	...	7·6	1·0
3.	4 to 6 feet from tip of main vine	...	...	...	...	8·4	·8

There is little to be remarked about the figures obtained for ether extract, nor would it be expected that anything of importance would become clear from an estimation of the



heterogenous mass of substances extracted by ether. The determination of essential oil gives results, however, of decided interest. The leaves from the upper part of the plant, in each case contain more essential oil than those in the lower part of the plant. This is particularly marked in the leaves on the branches. While the leaves at the bottom of the main stem contain 70 per cent. of the essential oil in those near the top, the leaves on the lower branches only contain 44 per cent. of those on the branches near the top. The gradual diminution of essential oil as one goes down the plant is interesting in view of the fact that young leaves near the top of the plant are not considered good for chewing, though (as we shall see later), it is undoubtedly the essential oil which gives the leaves their chief value. There is evidently some other constituent or condition in the younger leaves which neutralises the effect of the larger amount of essential oil. What this is, we have no information at present.

#### 5. *Tannin*—

When these investigations were commenced, we had an idea that the astringency of the leaves had something to do with their value, and hence the estimation of that class of substances which may be taken together as 'tannin' was of very considerable interest. The figures obtained were, however, as follows :—

					Tannin.	
					Per cent.	
I. Leaves from the main vine—						
(1)	Within two feet of tip	...	...	...	·97	
(2)	2 to 4 feet from tip	...	...	...	1·24	
(3)	4 to 6 feet from tip	...	...	...	1·17	
II. Leaves from the branches—						
(1)	Within 2 feet of tip of main vine	...	...	...	1·05	
(2)	2 to 4 feet from tip of main vine	...	...	...	1·30	
(3)	4 to 6 feet from tip of main vine	...	...	...	1·11	

The figures obtained do not show much variation in the amount of tannin in the different parts of the plant. But both the leaves from the main vine, and those from the branches do seem to indicate that the largest percentage of tannin sub-

stances are contained in the leaves from the middle of the plant. The younger leaves do not appear to have acquired their maximum amount: the older ones seem to have lost some of what they once possessed.\* This is curious from the fact that it is precisely these middle leaves which are most desired for chewing. The matter is one which demands further investigation, but, so far, we have not been able to spare time for it.

#### 6. *Acidity*—

The acidity found in the leaf did not vary very much according to the part of the plant from which the leaf was taken. The actual figures reported represent the number of cubic centimetres of caustic potash solution of "one-tenth normal" strength required to neutralise the acidity of the leaf. They are as follows:—

				Acidity.
				(Cubic centimetres of $\frac{N}{10}$ caustic potash required for 100 grammes dry leaf).
I. Leaves from the main vine—				
(1)	Within two feet of tip	...	...	56 cc.
(2)	2 to 4 feet from tip	...	...	60 cc.
(3)	4 to 6 feet from tip	...	...	58 cc.
II. Leaves from the branches—				
(1)	Within 2 feet of the tip of the main vine	...	...	56 cc.
(2)	2 to 4 feet from tip of main vine	...	...	62 cc.
(3)	4 to 6 feet from tip of main vine	...	...	60 cc.

#### 7. *Diastatic Activity*—

The figures which follow, indicate the number of grammes of starch which will be converted into maltose by 100 grammes of the dried leaf in forty-eight hours. It will easily be seen that this figure may be of importance in view of the general reputation of betel-vine leaves as a digestive agent. The actual figures

\* These results are interesting when compared with those obtained for tea, the only other plant we know which has been investigated in this sense. In that plant the youngest leaves contain far the largest quantity of tannin substances,

are as follows, the leaves being gathered in the morning, about 10 A.M.

				Diastatic Activity.
I. Leaves from the main vine.				
(1)	Within 2 feet of tip ...	...	...	12.3
(2)	2 to 4 feet from tip ...	...	...	12.1
(3)	4 to 6 feet from tip ...	...	...	4.5
II. Leaves from the branches.				
(1)	Within 2 feet of tip of main vine ...	...	...	14.3
(2)	2 to 4 feet from tip of main vine ...	...	...	8.5
(3)	4 to 6 feet from tip of main vine ...	...	...	7.0

It is difficult to see a relationship between the use for chewing and the diastatic activity. The lower, harder, and older leaves naturally contain less diastase, and are recognised as unsuitable for use. The middle leaves are the best for chewing,—better than the younger leaves on the plant. This does not seem to correspond in any way with the diastatic activity. The diastase is far more variable than the amount of starch on which it acts.

Such are the general characters of the leaves obtained from different parts of the betel-vine at the same time. The younger leaves on the plant contain much more essential oil, much more diastase, and much more sugars than those which are older. On the other hand the tannin does not vary in this direction. The leaves both on the middle branches and on the middle part of the main vine contain slightly the largest quantity of 'tannin.' To go further than this in regard to the causes of the universal use of betel-vine leaves and the reason for which they are eaten demands a comparison of leaves more or less highly appreciated. The study of the production of the so-called 'bleached' leaves, which are about three times the value of ordinary green leaves, promised to give results in clearing up this question. Their study was, therefore, taken up in considerable detail.

## III.

THE COMMERCIAL BLEACHING OF THE BETEL-VINE LEAF, AND THE  
CHEMICAL CHANGES BY WHICH IT IS ACCOMPANIED.

It is well known that although the leaves of the betel-vine are eaten in their fresh condition in by far the majority of cases, yet this is not the state in which they are most appreciated, at any rate in Western India. When required for special occasions or by those who can pay the extra price demanded, they are used in the bleached condition. That is to say, they are prepared in such a fashion that the larger part of the chlorophyll apparently disappears, the leaves become quite tough but flaccid, and they appear almost of the colour of leaves etiolated by being grown in the absence of light.

This process of bleaching betel-vine leaves has never, so far as we can find, been the subject of any investigation. That storehouse of information, Watt's Dictionary of the Economic Products of India, although it devotes seven pages\* to the description of the leaves of the betel-vine, their preparation and their uses, does not even mention the fact that they are bleached. The same is the case also with the same author's more recent book on the Commercial Products of India, † and other authors are equally silent. And yet the process is the basis of a very considerable industry carried on by a special class of people who keep their processes secret with very great care. Most of the people, at least in the neighbourhood of Poona, are Mohamedans called *Tāmboli* or more commonly *pan-bhātivalas*.

The result of bleaching is a very great increase in the value of the leaves. The actual price paid for leaves of various kinds in the Poona bazaar for a number of months has been ascertained and is given in the table opposite.

We have had the advantage of being allowed by one of the members of this community to follow his system carefully, and are hence able to present here the actual methods which he

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\* Vol. VI, Part I, page 247.

† Pages 891–896.



employs. We have also followed the process by analysis with reference to several of the important constituents, and are able to give in addition an account of the variation in these constituents throughout the process.

The leaves of the betel-vine to be used for bleaching should best be obtained from a garden of at least three years' standing, and the best results are obtained with leaves from a garden four to seven years old. This ensures that the vines are of older growth and the leaves well developed. These leaves should not be very tender, or inferior results are obtained. In buying the leaves for bleaching,—for the bleachers are always different people from the growers,—attention should be paid to the colour, especially in the case of leaves from vines which have been recently earthed up, and new growth produced (*navati* leaves). The colour should be a dark green, rather darker than usual, and not on any account a light green or *gajrya*. These light coloured leaves are useless as they often rot during the bleaching process. The midrib should be prominent and the stalk and surface of the leaves should be rather rough to the touch. These are of course the practical tests, but the eye of experience is quite sufficient to detect a good lot of leaves for the purpose.

Not only, according to the growers, is the actual character of the leaves important, but the season in which they are taken. In the cold weather, and especially in the months of November, December, and part of January the growth of the leaves is very slow and they give poor results when they are bleached. During this season the leaves rot rather than bleach. The commencement of the hot weather gives the best results. From the end of March to May the coiling of the creeper takes place, and at that time the most suitable leaves (*junawan*) are available in smaller quantities and are very dear. In fact, all leaves are more scarce at this time of year than at any other. From May onward the new leaves (*navati*) begin to appear in the market. These are useless for bleaching until they become dark in colour with increasing age. Then they improve in quality. By July

they can be used for the purpose, and from August and onward they are quite in good condition like the *junawan*.

The method of bleaching is as follows: One *kudtan*, or from fifty to seventy pounds of leaf is bleached at one time. This *kudtan* contains forty-one *kavalis*, each containing four hundred leaves, so that a *kudtan* contains about 16,400 leaves. The packing of the leaves in the *kudtan* is peculiar, but quite systematic, and is exactly similar to that used in packing betel leaves for transit. The stalks of the leaves should be cut close to the base of the leaf. A special instrument is used for this purpose but scissors answer the same purpose.

A large round basket from two to two and a half feet in diameter and twelve to eighteen inches high is selected and lined with matting. If a smaller number of leaves are to be bleached at once the height should be greater and the diameter less. There is nothing special in the form or material of the basket and a galvanised iron pot is often used. In this case, though the process is more rapid, a larger proportion of the leaves become rotten. In this case plantain leaves are spread at the sides and bottom of the vessel.

Usually after lining the basket with matting and a few plantain leaves inside this, water is sprinkled to wet these leaves. Then betel leaves with stalks duly cut off are arranged in layers, the leaves being almost vertical, but lying slightly over one another, the underside uppermost, as in the ordinary packing of such leaves for transit. Each layer is in the form of two or three circular rings of leaves. A vertical hole is reserved in the centre of convenient diameter to allow the hand when introduced to reach the bottom layer easily. This enables a constant watch to be kept over the process. The leaves in each layer usually amount to two thousand five hundred. After each layer is complete one to two pounds of water is sprinkled carefully over all the leaves in the layer. In all ten to twelve pounds of water or fifteen pounds at the utmost are sprinkled over one *kudtan* of leaves,—at least, this is the quantity in the hot weather. In the rainy season the amount used is less, as the

leaves then are more watery, and reaches five to ten pounds in all. Experience, however, is said to be the only guide as to the exact amount to use: the larger the amount of water used, the more rapid is the bleaching. In this case, however, there is much more rotting among the leaves, and a slow bleaching is always preferred. These quantities apply to *junawan* leaves: *navati* leaves require less water. Any excess of water gradually drains away.

There are several other methods of wetting the leaves, and the manner in which it is done is evidently a matter of detail. Sprinkling, however, is considered best, as leading to a slow, normal bleaching, with very few rotten leaves.

The basket is then covered with a wet gunny bag and kept in a warm, ventilated place,—where there is no chance of sunshine. In this state the basket should be kept for three or four days according to season. On the third or fourth day the gunny bag is removed and the state of the leaves observed. They are examined to see whether the water added is sufficient or in excess, as also to note whether there has been any sudden rise in temperature. After about eight days all the leaves are taken out, carefully examined and any which have commenced to rot removed. If the colour of the leaf near the base becomes red or reddish brown, it should at once be rejected. A yellow colour or a turmeric colour anywhere on the leaf is very objectionable. Leaves with clear spots of this colour are also removed.\*

At this stage there are a few leaves which have bleached properly and these are taken out for use, and the remainder arranged in the *kudtan* as before. No more water is now added, but the plantain leaves at the bottom are again wetted. The whole mass may now be weighed and covered by a wet gunny bag as usual.

The taking out and picking over is repeated every five or six days, and at every stage more leaves are bleached. If a longer time is allowed to elapse, a large number quickly become rotten.

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\* This objectionable colour is classed as Indian yellow (*Jauve indien*) in the colour scale published by the Société française des chrysanthemistes and prepared by R. Oberthür.

In the hot weather almost all that are likely to give good results have bleached in ten to twelve or fifteen days ; in the cold weather they are kept for fifteen to twenty days, or even longer than this,—and yellow rather than white leaves are usually obtained.

The process of selecting and turning the leaves is considered extremely important as after the first few days more and more of the leaves begin to rot, and this rotting quickly spreads to the other leaves. If it is required, by continuous turning a large proportion of the leaves can be kept good for two months.

The colour to be desired in the final product is that termed *jaune soleil* or sunflower yellow in the colour scale previously referred to. Highly bleached leaves sometimes reached an *amber white* (*blanc ambre*) on the same colour scale. Properly bleached leaves should be very soft, tender, of the proper colour, but very bright, clear of any stain as if rotting had commenced, and they should further increase in brightness on keeping. A brittle leaf is not liked, and leaves too highly bleached are objected to.

The following is an account of an actual experimental bleaching under our observation.

The *bhati* was set on June 11th, 1911.

The first turning out and selection took place on June 16th, 1911. The leaves which showed an Indian yellow colour were thrown aside for use at once. They are called 'dead' and are utterly useless for further keeping. The rotted ones were thrown out as well as those which had begun to turn brown at the base. Those which had begun to turn brown at the tapering end were kept after removing the rotted part. Nearly ten per cent. of the leaves became useless for further bleaching. Practically no leaves showed any sign of real bleaching. Among *navati* leaves, there was no change at all except a duller appearance.

The second, third, and fourth turnings which followed every fifth or sixth day were carried out in the same way. No further water was applied except the wetting of the plantain leaves at the bottom of the basket, and of the gunny bag with which the *kudtan* was covered. The basket was kept in a cool place. The



colour showed progressive changes from the fresh green of the original leaves to a fully bleached colour.

On the fifteenth day all the leaves were bleached, except those which had become rotten or were considered as unlikely to bleach if kept further.

This was the process as carried out by the *Tamboli* and it seemed so simple that the next step was to carry out the bleaching ourselves under conditions where the control could be more perfect and the process could be watched with greater care. Leaves were therefore brought from a *pan* garden packed in the ordinary *kudtan*. The leaves contained in the *kudtan* and few others after removal of the stalks weighed twenty-three kilogrammes about, while the stalks removed weighed six kilogrammes. The number of leaves was approximately sixteen thousand.

The *bhati* was started on November 1st, 1911, in a basket of the form ordinarily used for this purpose. It was lined with plantain (*vawali*) leaves as usual at the bottom of the basket. Two pounds of water were required to moisten these.

The leaves were then arranged in the usual way, packed almost vertically side ways, but slightly leaning over so that the lower side of the leaf faced uppermost. One pound of water was sprinkled over each layer and thus five pounds for the whole *bhati* of leaves. The whole was then covered by a wet gunny bag in the approved style to stop evaporation and, as the people say, to maintain the temperature of the *bhati* as far as possible. The leaves when taken for the bleaching process were not dry as the *kudtan* containing leaves had been a short time previously soaked in water and hence very little water was required. The leaves were in excellent condition for bleaching. Four days later the leaves were all examined and repacked, not this time so much to pick out the bleached leaves as to see whether the water added was sufficient or in excess and also to see if there had been a sudden rise in temperature.

This examination is stated to be necessary for if the water added be too large in amount, the temperature rises, the leaves

become dark in colour, rot quickly and do not bleach well. If the amount of water is too small, the bleaching is uneven and the leaves are apt to dry, which is fatal. In the present case the leaves were rather dry and four pounds of water additional were added to the *bhati*. There was no change in the colour of the leaves and no great increase in temperature.

On November 10th—ten days after the leaves were put to bleach—they were turned for the first time in order to remove the leaves wholly or partially rotten and others which were useless for further keeping, as well as any which may be already bleached. The following were the actual figures obtained :—

*November 1st, 1911.*

Total Weight	...	...	...	...	23,080 grammes.
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*November 4th, 1911.*

Total Weight	...	...	...	...	22,400 „
Leaves removed rotting	...	180	grammes.		
Weight of leaves remaining	...	22,220		„	

*November 10th, 1911.*

Total Weight	...	...	...	...	21,820 „
Leaves bleached and fit for use	...	1,130	grammes.		
Leaves partially bleached	...	4,540		„	
Leaves not yet bleached	...	13,560		„	
Partly or wholly rotten and hence removed	...	2,490		„	

The extent to which the decay had gone in the leaves removed rotting, was as follows :—

Leaves rotten throughout	...	30	grammes.
Leaves rotten at the tip only	...	1,750	„
Leaves rotten at the stalk only	...	167	„
Leaves, not rotten, but showing signs of incipient decay	...	543	„

In rearranging the leaves the whole of the rotten and of the bleached leaves were removed and samples amounting respectively to 500 grammes of unbleached leaves and 906 grammes of partially bleached leaves were taken, and, as is usual, the layers which had previously been uppermost were put at the bottom. The total weight of leaves placed in the *kudtan* again was 16·78

kilos. As the temperature was low, the leaves were not again examined, turned and repacked until November 16th. This second turning with the third is supposed to give the best bleached leaves. The actual figures obtained of the second turning, *i.e.*, on November 16th are given below :—

*November 16th, 1911.*

Total Weight	...	...	...	...	15,770 grammes.
Leaves bleached and fit for use	...	3,920	grammes.		
Leaves not yet fully bleached and fit for further keeping	...	9,320	"		
Leaves partially or wholly rotten	...	2,530	"		

The extent to which the decay had gone in the leaves removed as rotting was as follows :—

Leaves rotten throughout	...	223	grammes.
Leaves rotten at the tip only	...	1,242	"
Leaves rotten at the stalk only	...	680	"
Leaves not rotten, but showing signs of incipient decay	...	380	"

In again rearranging the leaves the whole of the rotten leaves and of the bleached leaves were removed, and a sample amounting to 1,950 grammes of the unbleached leaves was taken out for examination. The total weight of leaves replaced in the *kudtan* was 7,370 grammes. The next examination took place on November 21st, 1911, and resulted as follows :—

*November 21st, 1911.*

Total Weight	...	...	...	...	6,750 grammes.
Leaves bleached and fit for use	...	3,200	grammes.		
Leaves not yet fully bleached, and fit for further keeping	...	2,400	"		
Leaves partially or wholly rotten	...	1,150	"		

The extent to which the decay had gone in the leaves removed as rotting was as follows :—

Leaves rotten throughout	...	200	grammes.
Leaves rotten at the tip only	...	500	"
Leaves rotten at the stalk only	...	450	"

In arranging again the small quantity of leaves for further bleaching, care had specially to be taken to avoid the possibility

of drying. The total weight of leaves replaced in the *kudtan* was 2,700 grammes. They were again examined on November 30th, as follows :—

November 30th, 1911.

Total Weight	...	...	...	2,590 grammes.
Leaves bleached and fit for use	...	1,170	grammes.	
Leaves not bleached and fit for further bleaching	...	360	"	
Leaves partially or wholly rotten	...	1,060	"	

The extent to which the decay had gone in the leaves removed as rotting was as follows :—

Leaves rotten throughout	...	410	grammes.
Leaves rotten at the tip only	...	130	"
Leaves rotten at the stalk only	...	520	"

This was the end of the process. The leaves which refuse to bleach can be sold cheaply as fresh leaves. Those which have rotten patches at the tip or the stalk have the rotten pieces removed, and are then sold as leaves of inferior quality.

The total result of this commercial bleaching of betel-vine leaves was as follows :—

Original weight of leaves	...	...	23,580 grammes.
(Leaves taken for samples	...	...	4,520 " )
			19,060 "
Actual weight of leaves obtained	...	...	16,210 "
Leaves bleached and fit for use	...	...	8,630 grammes.
Leaves which did not bleach	...	...	360 "
Leaves partly or wholly rotten	...	...	7,227 "
Actual loss in weight during bleaching	...	...	2,850 "
			19,067 "

The extent, taking the whole operation into account, to which the decay had gone in the leaves when removed was as follows :—

Leaves rotten throughout	...	...	865 grammes.
Leaves rotten at the tip only	...	...	3,622 "
Leaves rotten at the stalk only	...	...	1,817 "
Leaves removed as showing incipient rotting	...	...	923 "
			7,227 "

Of these all except the first would be saleable.



These results are shown in percentages in the following table :—

Date. 1911.	Kind of leaf and operations performed.	Not bleached. %	Partly bleached. %	Bleached. %	Partly or wholly rotten. %
November 1st ...	Fresh leaves ...				
" 10th ...	First turning of all the leaves.	62.5	20.7	5.2	11.6
" 16th ...	Second turning of the residue unbleached on 10th.	59.1		24.9	16.0
" 21st ...	Third turning of the residue unbleached on 16th.	47.4		35.6	17.0
" 30th ...	Fourth turning of the residue unbleached on 21st.	14.0		45.0	41.0

At the end of all the operations we have —

Unbleached leaves remaining ...	...	...	2.2 per cent.
Bleached leaves ...	...	...	53.3 "
Partially or wholly rotten leaves	...	...	44.5 "

Careful temperature records were kept in connection with this *bhati* which are given in the table opposite. It will be seen that the rise in temperature was very slight indeed, the loss of heat due to evaporation of the water almost counterbalancing the rise of temperature due to the changes which take place.

This is, by no means, the only *bhati* which has been carried through completely, but all give results which are comparable with those here quoted. There is no need to go into full details with regard to these, but summarised figures regarding one other will indicate how the process varies from season to season, and from condition to condition.

In the case which we shall now describe, *junawan* leaves considered particularly suitable for bleaching were taken on

March 9th, 1912. The progress is shown by the following figures :—

*March 9th, 1912.*

Total weight	...	...	...	...	27,820 grammes.
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*March 11th, 1912.*

Total weight	...	...	...	...	27,670 grammes.
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Leaves showing signs of incipient rotting and hence removed	...	...	670 grammes.
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Weight of leaves remaining	...	27,000	„
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*March 15th, 1912.*

Total weight	...	...	...	...	22,680	„
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Leaves bleached and fit for use	...	570 grammes.
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Leaves not bleached or partly bleached	18,710	„
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Partly or wholly rotten	...	3,400	„
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Total weight of leaves retained after turning*	...	17,680	„
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*March 21st, 1912.*

Total weight	...	...	...	...	16,230	„
--------------	-----	-----	-----	-----	--------	---

Leaves bleached and fit for use	...	3,500 grammes.
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Leaves not bleached and fit for further bleaching	...	...	12,070	„
---	-----	-----	--------	---

Partly or wholly rotten	...	660	„
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Total weight of leaves retained after turning ..	9,980	„
--	-------	---

*March 29th, 1912.*

Total weight	...	...	...	8,650	„
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Leaves bleached and fit for use	...	5,000	„
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Leaves not bleached or fit for further bleaching	...	...	2,150	„
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Partly or wholly rotten	...	1,500	„
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The total result of this commercial bleaching of this lot of betel-vine leaves was as follows :—

Original weight of leaves	...	...	27,820 grammes.
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(Leaves taken for samples	...	...	3,420 „ )
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24,400	„
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Actual weight of leaves obtained	...	17,450	„
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Leaves bleached and fit for use	...	9,070 grammes.
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Leaves which were not bleached	...	2,150	„
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Leaves partly or wholly rotten	...	6,230	„
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Actual loss of weight during bleaching	...	6,950	„
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24,400	„
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\* Large samples were taken from the leaves for analyses at each turning, and hence there appears to be a very large loss.

The extent, taking the whole operation into account, to which the decay had gone in the leaves when removed was as follows:—

Leaves rotten throughout	...	...	...	554 grammes.
Leaves rotten at the tip only	...	...	...	3,042 „
Leaves rotten at the stalk only	...	...	...	540 „
Leaves removed as showing incipient rotting	...	...	...	2,096 „
				<hr/>
				6,232 „

Of these, as already remarked, all except the first lot would be saleable.

At the end of all the operations we have, in percentages,

Unbleached leaves remaining	...	...	...	12.3
Bleached leaves	...	...	...	52.0
Partially or wholly rotten leaves	...	...	...	35.7

The temperature records in the above *bhati* are shown in the table opposite:—

In connection with these temperature records, it may be interesting to give figures indicating the rates of bleaching and of becoming rotten in the upper layer of leaves, and in the remainder of the basket.

*March 15th, 1912.*

		Upper layer.	Remainder of <i>bhati</i> .
Bleached leaves	...	2.9 per cent.	2.4 per cent.
Leaves not yet bleached	...	85.3 per cent.	81.9 per cent.
Leaves more or less rotten	...	11.8 per cent.	15.7 per cent.

*March 29th, 1912.*

		Upper layer.	Remainder of <i>bhati</i> .
Bleached leaves	...	54.2 per cent.	60.4 per cent.
Leaves not yet bleached	...	29.2 per cent.	21.8 per cent.
Leaves more or less rotten	...	16.6 per cent.	17.8 per cent.

These would seem to indicate that the higher temperature in the lower layers at the commencement of the process leads to an increase in the number of rotten leaves, but not to an increase in the amount of bleaching. At the latter part of the

process, when there was no difference of temperature, the bleaching went on a little more rapidly in the lower layers.

The progress of the bleaching process was followed at every stage by determination of the amount of the constituents which seemed likely to be important as indicated in Part II of the present paper. The methods there indicated were adopted in the estimation.

(1) *Sugars*.—The changes which occurred during the process are indicated in the following table :—

Date, 1911.	Character of sample.	Reducing sugars.	Non-reducing sugars.	Total sugars.
		Per cent.	Per cent.	Per cent.
November 1st ...	Fresh leaves ...	0.43	1.30	1.73
November 10th {	(a) Unbleached ...	0.43	0.70	1.13
	(b) Partially bleached ...	0.49	0.51	1.01
	(c) Bleached ...	0.83	0.50	1.32
November 16th {	(a) Unbleached* ...	0.50	0.71	1.21
	(b) Bleached ...	0.83	0.41	1.24
November 21st {	(a) Unbleached* ...	0.64	0.46	1.10
	(b) Bleached ...	0.82	0.33	1.15
November 30th {	(a) Unbleached* ...	0.76	0.37	1.13
	(b) Bleached ...	0.83	0.29	1.12

\* In this case all leaves not bleached enough for removal, and fit for further treatment have been classed as unbleached leaves.

These results seem very definite. There is a rapid loss of total sugars in the early part of the bleaching process. Thereafter the amount falls only very gradually. The character of the reducing sugars in the bleached leaves is wonderfully constant. Thus we have :—

LEAVES.	Reducing sugars.	Non-reducing sugars.	Total sugars.
	Per cent.	Per cent.	Per cent.
After ten days bleaching ...	0.83	0.50	1.32
After sixteen days bleaching ...	0.83	0.41	1.24
After twenty-one days bleaching ...	0.82	0.33	1.15
After thirty days bleaching ...	0.83	0.29	1.12

At all stages the reducing sugar seems to have reached a constant amount in the bleached leaves, the non-reducing sugar



being the constituent which gradually falls. At every stage, too, the leaves which have not bleached do not contain as much reducing sugar as, and do contain more non-reducing sugar than, the fully bleached leaves. The following figures from the leaves which did not bleach compare well with those last given :—

LEAVES.	Reducing sugars.	Non-reducing sugars.	Total sugars.
	Per cent.	Per cent.	Per cent.
After ten days bleaching ...	0.43	0.70	1.13
After sixteen days bleaching ...	0.50	0.71	1.21
After twenty-one days bleaching ...	0.64	0.46	1.10
After thirty days bleaching ...	0.76	0.37	1.13

At the end of the process it will be seen, however, that the character of the sugars in the leaves which refuse to bleach is gradually approaching that in the bleached leaves. It would appear, therefore, that with regard to the sugars an identical or similar reaction is taking place to that which has taken place in the bleached leaves,—but it goes on much more slowly.

(2) *Starch*.—The changes in the amount of starch are as interesting as those which take place in the sugars. The following table gives the actual figures obtained :—

Date, 1911.	Character of sample.	Starch. Per cent.
November 1st ...	Fresh leaves ...	3.10
November 10th ...	{ (a) Unbleached ... (b) Partially bleached ... (c) Bleached ...	3.07 2.90 2.89
November 16th ...	{ (a) Unbleached* ... (b) Bleached ...	2.46 1.92
November 21st ...	{ (a) Unbleached* ... (b) Bleached ...	2.68 1.90
November 30th ...	{ (a) Unbleached* ... (b) Bleached ...	1.52 1.44

\* In this case all leaves not bleached enough for removal, and fit for further treatment, have been classed as unbleached leaves.

The amount of starch gradually diminishes in all the leaves, whether they are bleaching or no. The loss of starch, however,

goes on much faster in the leaves which bleach than in those which refuse to do so, at any rate until the last stages of the process. At the second and third turning of the leaves a constant position of the starch seems almost to have been reached,—but this is shown not to be really the end of the process for a very considerable further reduction takes place after the twenty-first day.

Taking the figures for the sugars and the starch together we may say that in the *bhati* we are discussing—

(1) The reducing sugars rose to a constant amount in the bleached leaves.

(2) The non-reducing sugars suffered a constant decrease during bleaching.

(3) The starch suffered a constant decrease during bleaching.

(4) These changes invariably took place faster in the leaves which bleached easily than in those which would not do so.

Though the experimental *bhati* we have quoted and for which we have given the results is the most complete we have made, these same points with regard to the sugars and starch seem to be indicated in other cases in which we have carried out the process. The following are the figures obtained for a *bhati* worked from September 1st to 9th, 1911. In this case the leaves were *navati*, but were considered fit for bleaching. The leaves had been plucked several days before the *bhati* was set. This, however, is considered no disadvantage. The figures were as follows :—

Date, 1911.	Character of sample.	Reducing sugars.	Non-re- ducing sugars.	Total sugars.	Starch.
		Per cent.	Per cent.	Per cent.	Per cent.
September 1st	Fresh leaves	0.39	0.55	0.94	2.01
September 9th	{ (a) Unbleached	0.40	0.51	0.91	1.96
	{ (b) Bleached	0.28	0.25	0.53	1.64
September 14th	{ (a) Unbleached	0.32	0.37	0.69	1.70
	{ (b) Partially bleached	0.34	0.27	0.61	1.73
	{ (c) Bleached	0.40	0.30	0.71	1.51
September 19th	{ (a) Unbleached	0.36	0.45	0.81	1.16
	{ (b) Bleached	0.39	0.38	0.77	1.01

Here, though the condition of the leaf at the beginning with regard to the content of sugars and starch precluded apparently the striking results obtained with regard to the reducing sugars in the former case, yet in nearly all other particulars the results agree with the conclusions above given. There is the reduction in the amount of starch, the reduction in the amount of non-reducing sugars, taking place more rapidly, as a rule, in the bleached than in the unbleached leaves, and the fact that the reducing sugars do not decrease,\* although they do not increase as in the *bhati* previously reported.

The results of a third *bhati* may also be reported, taken at an even more favourable season than the last two, and with *junawan* leaves, considered specially suitable for bleaching. The *bhati* was set on June 13th, and lasted till June 27th, and so far as sugars and starch were concerned, gave the following results:—

Date.	Kind of Leaves.	Reducing sugars.	Non-re- ducing sugars.	Total sugars.	Starch.
June 13th ...	Fresh leaves ...	Per cent. 0·53	Per cent. 0·97	Per cent. 1·50	Per cent. 1·78
June 16th ...	{ (a) Unbleached ... (b) Showing signs of bleach- ing ...	0·74 0·74	0·62 0·82	1·36 1·56	1·80 1·70
June 19th ...	{ (a) Unbleached ... (b) Bleached ...	0·56 0·62	0·97 0·42	1·53 1·04	1·34 1·76
June 23rd ...	{ (a) Unbleached and parti- ally bleached only ... (b) Bleached ...	0·88 0·96	0·43 0·40	1·31 1·36	0·91 0·92
June 27th ...	{ (a) Unbleached and partly bleached only ... (b) Bleached ...	0·75 0·95	0·35 0·29	1·10 1·24	0·86 0·73

Again the results are, on the whole, similar to what we have seen in the previous cases.

(3) *Tannin*.—We may now turn to a consideration of what happens to the tannin during the process of bleaching. The method of estimation is, no doubt, an imperfect one, but it represents, at any rate, the changes taking place in a particular class of substances, if not in any one chemical individual.

\* Omitting the analysis of the bleached leaf on September 9th which seems peculiar, and which we cannot account for.

(a) *Bhati set on November 1st, 1911.*

Date.		Kind of Leaves.				Tannin.
						Per cent.
November 1st	...	Fresh leaves	...	...	...	2.05
November 10th	{	(a) Unbleached	...	...	...	2.00
		(b) Partially bleached	...	...	...	2.00
		(c) Bleached	...	...	...	1.63
November 16th	{	(a) Unbleached	...	...	...	1.84
		(b) Bleached	...	...	...	1.87
November 21st	{	(a) Unbleached	...	...	...	2.10
		(b) Bleached	...	...	...	1.63
November 30th	{	(a) Unbleached	...	...	...	1.62
		(b) Bleached	...	...	...	1.89

(b) *Bhati set on June 13th.*—These leaves were in excellent condition for bleaching.

Date.		Kind of Leaves.				Tannin.
						Per cent.
June 13th	...	Fresh leaves	...	...	...	1.81
June 16th	{	(a) Unbleached	...	...	...	1.79
		(b) Partially bleached	...	...	...	1.70
June 19th	{	(a) Unbleached	...	...	...	1.84
		(b) Bleached	...	...	...	1.92
June 23rd	{	(a) Partially bleached	...	...	...	1.79
		(b) Bleached	...	...	...	2.07
June 27th	{	(a) Partially bleached	...	...	...	1.80
		(b) Bleached	...	...	...	2.03

(c) *Bhati set on September 1st.*—These leaves were of *navati* type, but were considered good enough for bleaching.

Date.		Kind of Leaves.				Tannin.
						Per cent.
September 1st	...	Fresh leaves	...	...	...	1.01
September 9th	{	(a) Unbleached	...	...	...	1.05
		(b) Bleached	...	...	...	1.32
September 14th	{	(a) Unbleached	...	...	...	1.03
		(b) Partially bleached	...	...	...	1.18
		(c) Bleached	...	...	...	1.36
September 19th	{	(a) Unbleached	...	...	...	1.10
		(b) Bleached	...	...	...	1.23



(d) *Bhati* set on November 13th, with *navati* leaves usually considered as unfit for bleaching. They bleached very badly.

Date.	Kind of Leaves.				Tannin.
November 13th	...	Fresh <i>navati</i> leaves	...	...	Per cent. 3.26
November 16th	...	No change in colour	...	...	2.03
November 19th	...	Leaves slightly changing in colour	...	...	2.05
November 23rd	...	Leaves slightly changing in colour	...	...	2.32
November 27th	...	Leaves bleached	...	...	2.38

These results, taken as they are from leaves bleaching in various times of the year, and under very varying conditions do not seem to indicate any very large change in the percentage of tannin in the process. In fact the actual figures would seem to indicate no relationship between the bleaching and the percentage of tannin whatever. Certainly the extra value of the bleached leaves does not depend on any increase of astringency due to increase in the amount of tannin.

Judged from a wider standpoint, these figures do not indicate any tendency of the tannin to disappear by any process of auto-digestion in these leaves, separated as they are from their plant, and yet still living,—nor on the other hand do they indicate that the tannin is a waste product which they produce,—or else one might expect under these conditions that the tannin would markedly increase.

4. *Ether Extract.* }
5. *Essential Oil.* }

The figures which we can present with regard to the ether extract and the essential oil date from more recent *bhaties* than those which have furnished the results for starch, sugar and tannin. The actual data here given are obtained from the process set on March 9th, 1912, with *junawan* leaves of the best kind, most suitable for bleaching.

Date, 1912.	Kind of Leaves.				Ether Extract. Per cent.	Essential Oil. Per cent.
March 9th	...	Fresh leaves	...	...	15.7	1.23
March 13th	{	(a) Unbleached leaves	...	...	13.1	1.26
		(b) Partly bleached leaves	...	...	12.9	2.23
		(c) Bleached leaves	...	...	13.0	4.76
March 21st	{	(a) Unbleached leaves	...	...	13.5	1.41
		(b) Bleached leaves	...	...	13.7	5.20
March 24th	{	(a) Unbleached leaves	...	...	14.3	1.28
		(b) Bleached leaves	...	...	13.5	4.20

We shall have no more to say with regard to the total ether extract. It evidently indicates nothing which is important from the present point of view. But the figures for the essential oil are very striking indeed. During the bleaching process,—and evidently intimately connected with the bleaching itself, there is a very large increase in the amount of essential oil. In one case it actually becomes four times as great in amount as it was in the original leaf, while in the leaves which refuse to bleach it remains almost constant in amount throughout.

This result is, in accordance, of course with the view that the essential oil is the constituent which gives their main value to betel-vine leaves, for the bleached leaves are usually worth three times at least as much as the fresh leaves.\*

Considered as a point in plant physiology, it is difficult to explain, but it might be worth while to draw attention again to the fact that one of us (H. H. Mann) found a considerable increase in the essential oil of the tea leaf during the "withering" or rather 'wilting' process in the manufacture, which has certain analogies with the process of bleaching which we are discussing.

The increase in essential oil during the bleaching of the leaf was so striking that it seemed worth while to see if a microscopic examination of the leaf would indicate in what way the increase in oil occurred. Sections of the fresh and bleached leaf

\* *Vide* above for prices in Poona Bazaar.

were, therefore taken,—and the following observations were made.

*Fresh Leaves.*—In these there were two kinds of oil globules, one type much larger than the other. The larger ones were transparent and seen in all parts of the leaf and were about 0.4 millimetre in diameter. The small ones were semi-transparent, and were seen all over the surface, were quite circular or elliptical, and were surrounded by chlorophyll grains, and were about 0.1 millimetre in diameter.

*Bleached Leaves.*—In these the small oil globules had become very much more numerous than before, and were clearly seen all over the surface. The larger globules were not affected, and their appearance and number remained very similar to what had been seen in fresh leaves.

6. *Acidity.*—The acidity, determined as previously indicated and expressed as the number of cubic centimetres of one-tenth normal caustic potash solution required to neutralise the acidity in one hundred grammes of leaves, is shown in the various stages of a typical *bhati* in the following table :—

Date, 1911.	Kind of Leaves.					Acidity (as above defined).
November 1st ...	...	Fresh leaves	...	...	...	112.8
November 10th	{	(a) Unbleached	...	...	...	108.0
		(b) Partially bleached	...	...	...	97.0
		(c) Bleached	...	...	...	120.0
November 16th	{	(a) Unbleached	...	...	...	85.0
		(b) Bleached	...	...	...	150.0
November 21st	{	(a) Unbleached	...	...	...	93.0
		(b) Bleached	...	...	...	161.0
November 30th	{	(a) Unbleached	...	...	...	115.0
		(b) Bleached	...	...	...	180.0

These figures are striking. The bleaching is accompanied by a very large increase of acidity, which becomes greater the longer the time the bleaching takes. In the leaves which do not bleach, the fact of keeping leads to little or no increase in acidity.

7. *Diastatic Activity*.—The following figures were obtained from a *bhati* conducted early in 1912 :—

Date.			Kind of Leaves.				Diastatic activity.*
March 9th	...	...	Fresh leaves	...	...	...	24.8
March 15th	...	{	(a) Unbleached	...	...	...	23.4
			(b) Partially bleached	...	...	...	15.5
			(c) Bleached	...	...	...	14.8
March 21st	...	{	(a) Unbleached	...	...	...	16.7
			(b) Bleached	...	...	...	11.5
March 24th	...	{	(a) Unbleached	...	...	...	15.6
			(b) Bleached	...	...	...	12.4

There is evidently a rapid reduction in the diastatic activity of the leaves during keeping under the conditions of the *bhati*, whether bleaching takes place or not. But this reduction is far more rapid, and goes much further when the bleaching is taking place than when this is not the case. This is perhaps what might be expected. The leaf is dying, though in the present case the process is very long,—and it is only natural that a product so characteristic of the living plant, and so intimately connected with the life processes of the leaf should be rapidly reduced during a process like that of bleaching.

8. *Nitrates*.—The determination of nitrates in leaf during the process of bleaching has led to some very curious results, indicating that the process which goes on is by no means always the same. In a *bhati* set in on August 5th, 1912, the following figures were obtained :—

Date.			Kind of Leaves.				Potassium Nitrate.
							Per cent.
August 5th	...	...	Fresh leaves	...	...	...	1.07
August 8th	...	...	Unbleached	...	...	...	1.06
August 12th	...	{	(a) Unbleached	...	...	...	1.00
			(b) Very slightly changed in colour	...	...	...	.90
			(c) Partially bleached	...	...	...	1.00
			(d) Bleached (white)*	...	...	...	.90

\* For a definition of what is meant by these figures *vide supra*.



Date.	Kind of Leaves.	Potassium Nitrate.
		Per cent.
August 17th ...	(a) Unbleached ...	74
	(b) Very slightly changed in colour ...	95
	(c) Partially bleached ...	1.05
	(d) Bleached (white)* ...	1.05
August 22nd ...	(a) Very slightly changed in colour ...	1.07
	(b) Partially bleached ...	1.06
	(c) Bleached (white)* ...	1.17
	(d) Bleached (yellow)* ...	0.04
August 25th ...	(a) Partially bleached ...	0.98
	(b) Bleached (white)* ...	1.09
	(c) Bleached (yellow)* ...	0.20

\* For a definition of what is meant by these figures *vide supra*.

With the exception of one case, of which we will speak directly, the effect of the process we are discussing on the quantity of nitrates in the leaf seems very small indeed. The fresh leaves taken contained slightly more than at almost any subsequent stage of the process. But the difference is small, and one might consider that in a normal bleaching process the nitrates remained unaffected.

In every bleaching process, however,—and more so in the cold weather when bleaching does not take place normally,—a few yellow leaves appear instead of white ones. They are looked on with great disfavour by the *tambolis*, and only command a very poor price in the market compared with those lighter in colour. We hardly suspected, however, how different was the process in the case of these leaves until certain variations in the amount of nitrate in bleached leaves called our attention to it. It was then found, in fact, that while the nearly white, normally bleached leaves contained about the same quantity of nitrates as the original leaves, in the yellow ones the nitrates had practically disappeared. Thus in the above table we have—

		Per cent.	
August 22nd ...	{ White leaves	1.17	KNO <sub>3</sub>
	{ Yellow leaves	0.04	KNO <sub>3</sub>
August 25th ...	{ White leaves	1.09	KNO <sub>3</sub>
	{ Yellow leaves	0.20	KNO <sub>3</sub>

These figures led to a closer investigation of the question in four different *bhatīs* with results given in the following table.

We have included the examination of some so-called *gajriya* leaves or leaves stated by the *tambolis* as not likely to bleach properly or at all :—

#### POTASSIUM NITRATE.

	First series.	Second series.	Third series.	Fourth series.
	Per cent.	Per cent.	Per cent.	Per cent.
Fresh leaves (fit for bleaching) ...	1.05	0.90	1.28	1.86
Fresh <i>gajriya</i> leaves (not fit for bleaching) ...	1.17	0.81	0.86	1.67
Bleached leaves, white ...	1.06	0.82	1.32	1.23
Bleached leaves, yellow ...	0.00	0.06	0.10	0.18

These figures confirm, in every particular, the experiment first quoted.

Such are the results obtained by following the process of conversion of green betel-vine leaves into the much more appreciated bleached leaves. In summary we may say that the process is accompanied—

- (1) by a very large increase in the amount of essential oil ;
- (2) by a very considerable increase in the acidity ;
- (3) by a disappearance of a large part of the starch and non-reducing sugars,—a disappearance which, however, is never complete ;
- (4) usually by an increase in the amount of reducing sugar ;
- (5) by no large change in the percentage of tannin ;
- (6) by no large change in the amount of nitrates in normally (white) bleached leaves, while the nitrates almost entirely disappear in the leaves which turn yellow during the process ;
- (7) by a large decrease in the amount of diastase.

#### ACTION OF VARIOUS GASES, VAPOURS, ETC., ON THE BLEACHING PROCESS.

At this stage it seemed possible that we might reach a better understanding of the bleaching process, and hence of the betel-vine leaf itself if we attempted to bleach the leaves in

presence of certain gases, or vapours,—or if they would not bleach, by leaving them in contact with such materials. In order to carry this out, a few leaves, usually five, were placed in a dish under a bell jar inside which the air was kept saturated with moisture by standing the bell jar in a dish of water. In the first experiments there was, in spite of all, a great tendency in the leaves to dry up. To avoid this, they were afterwards dipped in water before the experiment was started.

In the first instance, the changes in appearance produced by a number of strong re-agents were noticed for later guidance. The notes made regarding some of these are as follows :—

*Air and Water.*—No change was apparent either in colour or otherwise to the end of the second day, but on the third the fresh green colour was fading, and giving rise to a faint yellowish appearance. The following day the same change was progressing and bleaching had begun. On the fifth day, the leaves were half bleached to a more yellow tint than is normal, while a day later some of the leaves were more or less bleached, while they had begun to dry at the edge.

*Hydrogen Gas (moist).*—The leaves did not change in appearance and lustre for the first eight days. On the eighth day the leaves were slightly drying, but the fresh green colour remained. After fourteen days a slight change was seen in the colour. The original fresh colour was disappearing slowly, but beyond this the drying of the edges, etc., was the only noticeable change. A little later the leaves began to rot at the tips without any change in the green colour.

*Carbon Dioxide (moist).*—On the second day a slight brownish tinge appeared along the border and tip. On the following day the whole of the leaf was bordered by a dark coloured ring, but the general colour of the leaf was unchanged. On the fourth day the dark colour was extending all over the leaf, and slight rotting was noticed at the ends. A day later, the whole leaf had become of a dirty blackish green colour, destroying all lustre. The leaf was distinctly rotting in places.

*Oxygen (moist).*—The change described as occurring with air took place, but more rapidly with oxygen. On the fifth day the leaves had changed to yellow—the yellow colour being specially prominent at the stalk-end of the leaf. The day after, the leaves were yellow, and had become brittle. The change which had taken place differed in many respects, apparently, from a normal bleaching.

*Chlorine Gas (moist).*—Only a trace of chlorine was used, but the change was at once apparent. The leaves became reddish brown, all the green colour of the chlorophyll disappeared. They became very thin, changed to a yellow colour, then to brown, and then to white and semi-transparent.

*Dipping in Hydrogen Peroxide Solution and then moist air.*—Two strengths of solution were used containing respectively three per cent. and one per cent. of Hydrogen Peroxide. With the stronger solution the leaves changed rapidly in colour. On the second day small brown spots appeared everywhere on the surface while the veins had turned black. A day later all the spots had become black. On the fourth day the spots remained black, and the remainder of the leaf had become a faint yellow in colour.

The weaker solution had a very similar effect, but it appeared, of course, more slowly. A few brownish spots here and there were seen on the third day, while on the fourth day the leaves were becoming yellowish in colour. On the fifth day, when the observations terminated, the leaves had become more or less yellow, with a few brown specks, but still retained the lustre of the original leaf.

*Ammonia Gas.*—A very small quantity of ammonia solution was placed under the bell jar containing the leaves, and the effect noticed. On the second day, a yellowish tinge appeared on the leaves which changed gradually to brown, and on the following day almost the whole surface had become brown in colour. A day later the brown colour had become black, and in just a few places where this colour had not developed, the leaf had turned yellow, but it was in no sense a normal bleaching.

*Formic Acid Vapour.*—A small quantity of Formic Acid solution was placed under the bell jar.

On the second day big brown and dirty looking patches were seen on the surface of the leaves, while a day later these had extended, and occupied nearly the whole of the surface. On the fourth day, the leaf tips had become black, and the leaves had lost all lustre. The part which had not turned black or brown (a very small amount) was turning to a dirty yellow colour.

*Acetic Acid Vapour.*—This was used in the same way as Formic Acid vapour.

In this case the action was very rapid. After four hours the leaf had developed brown spots all over, and by the second day these had become brown, changing to black,—while almost all the surface was covered. On the third day, the leaf had lost all lustre and stiffness, looked as if scorched, and was rapidly turning black.

It was at once evident that the effect of some of these reagents was to kill the leaf at once, and the appearances which followed were simply the result of that death of the tissues. Moreover, it is evident that the effect of hydrogen was to prevent bleaching taking place. It appears in every degree probable that reducing agents, or even gases whose presence tends to prevent oxidation, tend to delay or hinder the process.

Further experiments were therefore made with a limited number of reagents as follows :—

- (1) Air and water vapour only.
- (2) Carbon Dioxide and water vapour.
- (3) Oxygen and water vapour.
- (4) Trace of Ammonia and water vapour.
- (5) Trace of Formic Acid vapour and water vapour.
- (6) Leaves dipped in 1 per cent. Hydrogen Peroxide solution and then kept with air and water vapour.

Several experiments were carried out, but the results obtained were so similar that to quote details of one experiment is to quote all. In this one case, the leaves were exposed to these



reagents on 14th June 1912, and the experiment lasted eight days. The daily temperatures at 1 p.m. were as follows:—

June 14th	...	...	29° C.
„ 16th	...	...	30° C.
„ 17th	...	...	30° C.
„ 18th	...	...	28° C.
„ 19th	...	...	29° C.
„ 20th	...	...	27° C.
„ 21st	...	...	27° C.

The appearances were as follows:—

*Air and Water Vapour.*—No change occurred for three days when the green colour of the fresh leaf seemed to be beginning to fade. A day later this was marked, and there was a yellowish tinge all over the leaves which seemed to be proceeding as in an ordinary bleaching operation. On the sixth day this change continued, and the loss of the green colour appeared quite regular, while by the following day some leaves were nearly bleached. A day later rotting had set in, and the operation was closed.

*Carbon Dioxide and Water Vapour.*—After two days little effect was visible except a very slight brownish tinge at the borders of the leaves, which was very marked two days later. At the same time the original green tint had become much darker in the leaves. Shortly afterwards the brownish tinge gradually extended to the remainder of the leaves, and by the seventh day rotting was visible at the ends of the leaf gradually extending to the middle by the eighth day.

*Oxygen and Water Vapour.*—On the fourth day bleaching became marked, and spread rapidly, commencing at the stalk end. This continued more rapidly than in the leaves exposed to air, and no rotting occurred till the seventh day, when one leaf showed signs of rotting from the stalk end. When the leaves were taken away on the eighth day, all had changed to yellowish white though not completely, but were rather brittle, and in this respect differed from ordinary well-bleached leaves.

*Trace of Ammonia and Water Vapour.*—After one day the leaf was noticed to be turning black at certain points, while small patches of brownish yellow colour appeared. Two days later, dirty black spots were seen all over. Some leaves had become blackish. The part not spotted or turned blackish seemed to be bleaching normally, and on the sixth day, was changing in colour to yellow. The colour was, however, an objectionable yellow, developing from the stalk end. All lustre was lost. No further change took place except the gradual rotting of the blackened and spotted part.

*Trace of Formic Acid Vapour and Water Vapour.*—On the second day, a brownish colour began to appear in large and small patches, which were, however, not by any means uniform. This rapidly extended all over the surface of the leaves, which turned a dirty blackish colour, with complete loss of lustre. Rotting rapidly set in, and mould began to grow on the leaves.

*Dipping in 1 per cent. Hydrogen Peroxide, and then keeping with Air and Water Vapour.*—No change occurred till the fourth day, when very small brown patches were seen on some parts of the leaves, while the original green colour was slowly fading over the remainder. The same condition persisted and progressed. Finally after eight days leaves fairly well bleached were obtained spotted over, in many parts, however, with black spots. The resulting leaves were very brittle.

Inasmuch as the increase in the essential oil seems to be the most important chemical change taking place during a normal bleaching, determinations were made of this constituent under the various treatments in special lots set on for this purpose. The results are shown in the following table :—

ESSENTIAL OIL IN DRY LEAF.

			Moist Air.	Carbon Dioxide.	Oxygen.	Trace of Ammonia.	Trace of Formic Acid.	Dipped in Hydrogen Peroxide.
			Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
After 24 hours	...	...	1.5	1.0	1.3	0.3	...	...
After 4 days	...	...	2.7	2.1	3.9	0.7	2.8	2.7
After 5 days	...	...	3.1	...	3.4	...	...	...
After 6 days	...	...	2.8	...	...	...	...	...

These figures show a gradual increase in the essential oil in moist air. It never reaches the proportion produced under the conditions of an ordinary *bhati*, but is in the same direction. With oxygen there is the same increase in the essential oil, which indeed reaches higher proportions than with air. Before the operations were stopped, however, the essential oil seemed to be again decreasing in amount.

With Carbon Dioxide, the increase in essential oil seems to be very much less.

The presence of a trace of Ammonia leads to the almost complete destruction of the essential oil. A trace of Formic Acid, on the other hand, does not seem to affect this, and the amount produced after four days is similar to that produced under the ordinary conditions with air.

Dipping in dilute Hydrogen Peroxide does not seem to have affected the development of essential oil.

As a whole, as a result of these experiments, it is evident that the process which takes place during bleaching is one of oxidation. Anything which prevents oxidation, prevents bleaching and prevents the development of essential oil. Moreover slight acidity is a necessary condition: the slightest trace of alkalinity (as with Ammonia Vapour) leads to the almost complete destruction of the essential oil and of the leaf.

Such are the results which we have obtained so far. As regards the commercial bleaching of the betel-vine we have shown how it is carried out, the conditions under which it is most successful, and in some measure the chemical changes by which it is accompanied. It remains to clear up more completely the nature of these changes, to examine more closely the manner in which the essential oil varies during the process, and to ascertain whether it is a change in kind as well as in quantity, and to investigate more closely the differences between leaves bleaching in different ways. Finally it is necessary to make further experiments to see whether the process can be expedited in any way

without loss in quantity in the final product, and so whether the present cumbrous and wasteful process cannot be modified so as to make it quicker, cleaner, and more satisfactory, leading to less loss of leaf through ordinary rotting and decay. We are actively continuing the work in these directions.





THE GASES OF SWAMP RICE SOILS :  
THEIR COMPOSITION AND RELATIONSHIP TO THE CROP.

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INTRODUCTORY.

IRRIGATED paddy or rice in South India is generally grown under swamp conditions throughout the growing season and in a puddled soil, *i.e.*, ploughed or levelled in water, but no general system of cultivation holds good, nor can it be said that what is found to be successful in one place will answer in another. On the South Malabar Coast, it is the general practice to plough the lands in the dry season with excellent results, but this same custom introduced into other districts has led to failure. Paddies which flourish in one delta or district often do not do so well when transferred to another place where the conditions are apparently of a similar character. Green-manuring is found to answer perfectly well in one area, but when tried in another area the crop fails. In one district the water may be run on to fields and the latter puddled and manured weeks before the crop is planted, but in other districts, the custom is to put in the green-manure just before the time of transplanting. These and the many other mutually opposed facts which can be quoted, make it essential that the conditions governing the growth of paddy should be closely studied in order to obtain,

if possible, some common basis capable of explaining them before material improvement can be made in paddy cultivation.

On considering the problem in all its general aspects, it was felt that a study of the soil gases formed the most promising field of enquiry, and the results obtained, as well as some from closely connected investigations, are detailed in the following pages.

Before proceeding to a consideration of the investigation, a brief description of the cultural conditions of Swamp Paddy Soils in South India will make clear the peculiar conditions under which the crop is grown and also clearly demark the scope of the enquiry and the application of the results.

In general, these soils are allowed to lie in an uncultivated condition during the hot season, during which period they dry to a considerable extent and, owing to their very heavy character, shrink considerably and wide cracks are formed reaching down to a depth of from two to three feet. This deep cracking of the soil leads to complete aeration, and no doubt nitrification proceeds apace at this time. On the South Malabar Coast, however, the land is systematically worked over during the dry season. As soon as water is available seed-beds are formed where the paddy germinates and grows until the time of transplanting arrives. Some time before transplanting water is admitted to the fields, which are then thoroughly ploughed and puddled, and the heavy crop of weeds formed on the dry soil is worked in. In addition, wherever available, large quantities of green-leaf manure are thoroughly incorporated with the soil by the trampling of cattle or coolies.

The amount of green-manure used varies with its availability and cost, but often the cultivators will scour the dry land for miles around to obtain it, and the use of as much as 4,000—5,000 lbs. per acre is quite common. In the deltas green-leaf manure is very scarce, and its use is not so common, but even there the seed-beds are heavily manured. In the Kistna Delta it is a common practice to sow sunn-hemp (*Crotalaria juncea*) just before harvesting the paddy and the resultant crop is used as fodder, but the straw and roots are ploughed into the soil.

After puddling and manuring the surplus water is allowed to drain off and the seedlings are transplanted. After transplanting, wherever the conditions permit, water is not allowed to stand in the fields until the seedlings are established, but care is taken to keep the moisture conditions such that no cracking or shrinking of the soil takes place. When the seedlings are established water is admitted in quantity and the whole of the fields are kept under water throughout the rest of the growing season, but, if possible, the land is drained just before harvest to permit of the drying off of the crop.

The main features, then, of paddy cultivation in South India are : (1) the maintenance of swamp conditions by the use of large quantities of water and by puddling the soil and so decreasing the natural drainage ; (2) the use of large quantities of green-manures. It is obvious that under these circumstances the soil conditions must be quite dissimilar to those obtaining in dry soils and that the course of the decomposition of the manure and the nutrition of the plant must also be very different.

## PART I.

### THE GASES OF THE SOIL, THEIR COMPOSITION AND RELATIONSHIP TO THE GROWTH OF THE CROP.

#### *The variations in the composition of the Soil gases.*

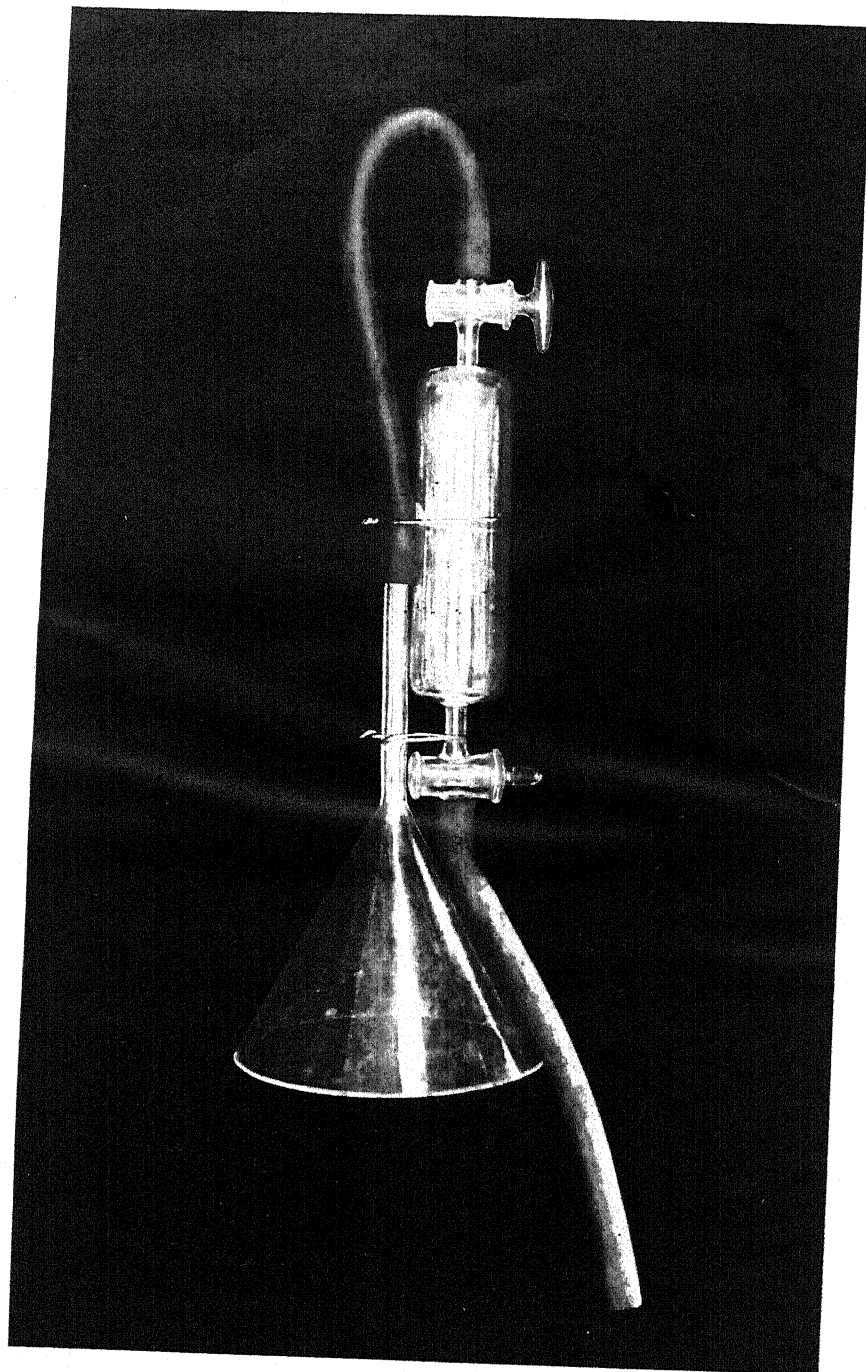
ON forcing a stick into the soil of paddy fields or on disturbing it in any other manner, bubbles of gas are given off which are easily collected and which on analyses are invariably found to consist mainly of Methane and Nitrogen. The proportion these gases bear to one another varies greatly, the Methane from about 15 to 75 per cent. of the total and the Nitrogen from about 10 to 95 per cent. In addition, Carbon-dioxide is generally present together with small amounts of Oxygen and Hydrogen. Other gases were tested for at intervals, but only those mentioned above have been detected. The amount of Carbon-dioxide present is, on the average, about 5 per cent., but this value may fall as low as 1 per cent. and rise as high as 20 per cent. The amount of Oxygen is usually only a trace, but values as high as 5 per cent. have occasionally been met with. Hydrogen is generally absent but as much as 10 per cent. has been recorded in uncropped plots.

Early in the course of the investigation, it was noticed that in cropped fields the proportion of Methane was generally low, whereas, in uncropped fields this gas greatly predominated and, consequently, the variations in the composition of the gas were particularly studied. To this end, a particular field was chosen and the gases were collected and analysed at intervals from the time of puddling in the green-manure to the time when the land was drained for ripening.

Several different methods of collecting the gas were tried, but the one found to answer best was to walk slowly across a field

Approximate number of persons in each group - 1000





Apparatus used for the collection of the Gases of Swamp Paddy Soils.

holding the apparatus figured in Plate I so that the funnel was always under the water. This apparatus consists merely of a large gas tube with a glass stop-cock at either end. The upper one is connected by means of a rubber tube to the collecting funnel, and to the lower one a piece of rubber tube is attached so as to permit of the water in the apparatus discharging below the surface of the water in the field. The whole is filled with water and that portion of the escaping gas collected by the funnel is conveyed to the gas tube, where it is easily isolated. The gases were collected by walking slowly across a field and holding the apparatus over the places of disturbance. This method of collection had the advantages, (1) that an average sample of the whole field was easily made and, (2) an approximate measure of the relative amounts of gas in the soil of different fields was obtained. The gas collected was conveyed to the laboratory and analysed at once. Several types of gas-analysis apparatus were used, but the one found most suitable was a modified form of Adeney's apparatus.

For the estimation of the Methane and Hydrogen, the method of exploding with Oxygen was mainly relied upon but the results were often checked by the method of combustion in a capillary platinum tube, especially when the proportion of Methane was low.

The results obtained during the year 1909 are tabulated below :—

TABLE I.

*Showing the composition of the gases from a cropped and manured field during the year 1909.*

Date.				% CH <sub>4</sub>	% N	% CO <sub>2</sub>	% O	% H
August	2nd, 1909	..	..	73.8	10.9	14.6	.7	Nil.
"	9th "	..	..	54.2	36.1	9.7	Nil.	"
"	16th "	..	..	67.4	21.4	11.2	Trace.	"
"	24th "	..	..	73.4	16.2	10.4	"	"
September	1st "	..	..	71.2	24.1	4.5	.2	"
"	18th "	..	..	64.3	26.5	9.0	.2	"
October	5th "	..	..	21.0	72.9	5.6	.5	"
"	26th "	..	..	21.4	67.7	10.7	.2	"
November	17th "	..	..	23.9	68.8	4.5	2.8	"

In this year, green-manure to the extent of 4,000 lbs. to the acre was ploughed in on July 27th, but the transplanting did not take place until September 7th, and during the whole of this period the percentage of Nitrogen remained low and that of Methane high. Some four weeks after transplanting, a decided change in the composition of the gas took place, and the Nitrogen, instead of being low as formerly, now predominated and continued so as long as it was possible to obtain samples of gas.

So far as it could be determined, the volume of gas in the soil was greater during the latter period, and it therefore appeared as if the presence of a crop brought about a loss of the Nitrogen of the soil and manure and also prevented the formation of Methane. Another important feature was that the soil conditions are anaerobic so long as water is over the surface. The fact that the presence or absence of a crop appeared to determine the composition of the soil gases was surprising, and consequently the experiment was repeated in 1910 on a different field with a different type of paddy, and the result was strictly parallel to the former experiment.

TABLE II.

*Showing the composition of the Soil gases in a cropped and manured field during 1910.*

Date.					% CH <sub>4</sub>	% N	% CO <sub>2</sub>	% O	% H
August	6th, 1910	..	..	..	66.2	11.0	20.9	1.9	Nil.
"	12th	"	..	..	71.3	12.2	16.5	Trace.	"
"	19th	"	..	..	56.3	37.1	6.6	"	"
"	26th	"	..	..	63.1	32.0	4.4	"	"
September	2nd	"	..	..	68.5	21.8	9.7	Trace.	"
"	9th	"	..	..	58.1	36.8	5.1	"	"
"	19th	"	..	..	57.4	35.9	6.7	"	"
October	1st	"	..	..	33.4	62.8	3.1	"	"
"	6th	"	..	..	18.5	78.1	3.2	"	"
"	14th	"	..	..	24.3	70.3	5.0	"	"
"	21st	"	..	..	17.2	76.9	5.6	"	"
November	5th	"	..	..	21.0	71.2	5.6	Trace.	"
"	11th	"	..	..	18.4	75.0	5.1	"	2.2
December	3rd	"	..	..	31.9	65.5	2.6	Nil.	1.5
"	10th	"	..	..	34.0	60.3	3.9	Trace.	Nil.
"	17th	"	..	..	36.3	60.3	3.4	Trace.	1.8
"	24th	"	..	..	38.6	59.4	2.0	Trace.	Nil.

CHART NO. 1.

DIAGRAM SHOWING THE VARIATIONS IN THE PERCENTAGE OF NITROGEN  
IN PADDY-SOIL GASES.  
%NITROGEN IN 1909 \_\_\_\_\_  
" " 1910 - - - - -

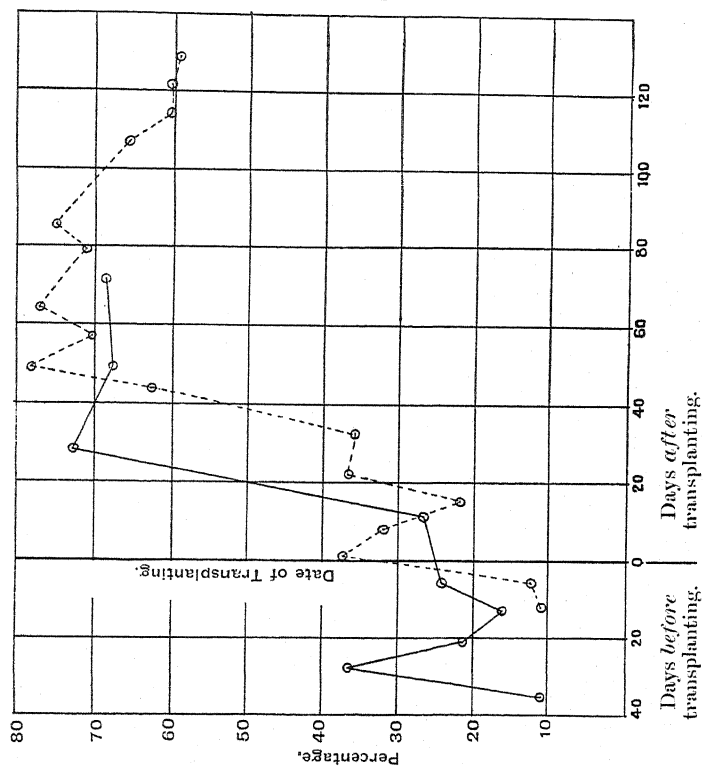
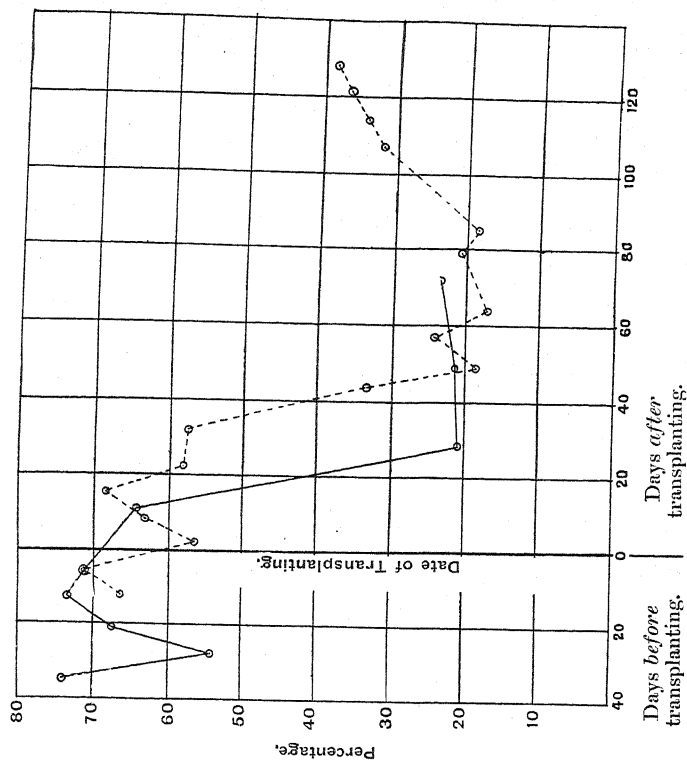


CHART NO. 2.

DIAGRAM SHOWING THE VARIATIONS IN THE PERCENTAGE OF METHANE  
IN PADDY-SOIL GASES.  
%METHANE IN 1909 \_\_\_\_\_  
" " 1910 - - - - -







This field was manured and puddled on August 3rd, and transplanting took place on August 18th. Here, again, the Methane predominates until the latter part of September, about 5 weeks after transplanting, but from then onwards the Nitrogen predominates.

The values for the percentages of Nitrogen and Methane obtained in these two experiments are plotted out in Charts Nos. 1 and 2, the dates in both cases being referred to the date of transplanting so that the curves are comparable. These curves show clearly the change in the composition of the gas about thirty days after the date of transplanting, but in order to make this point absolutely certain, the following experiment was carried out in 1911.

A small field was taken which had been under paddy cultivation for many years, and which in its known history had received no manure. Such a field has a very uniform texture and composition and is very well suited to experimental work on paddy. The field was divided into four plots by means of small earthen banks (bunds) and two of these plots were manured with green-manure to the extent of 8,000 lbs. per acre. The other two received no manure. Of the manured plots, one was cropped and one left uncropped and the gases from each were collected and compared. In the same way one of the unmanured plots was cropped and the other left uncropped. The gases were collected from all the plots on the same days and the results clearly show the influence of the crop on their composition. The manured plots will be considered first.

TABLE III.

*Showing composition of gases from the uncropped manured plot.*

Date.				% CH <sub>4</sub> .	% N	% CO <sub>2</sub> .	% O	% H
August	12th, 1911	..	..	58.6	35.6	1.7	2.2	1.9
..	26th	..	..	65.0	24.2	2.1	<i>Nil.</i>	8.7
September	2nd	..	..	64.4	20.1	3.0	1.0	11.5
..	9th	..	..	62.2	28.1	2.4	<i>Nil.</i>	7.3
..	16th	..	..	62.7	24.9	2.8	1.1	8.5
October	2nd	..	..	69.4	17.0	4.0	.8	8.8
..	9th	..	..	65.0	23.8	3.1	.8	7.3
..	24th	..	..	68.6	22.6	3.7	<i>Nil.</i>	5.1
..	31st	..	..	57.3	35.9	2.6	..	4.2
November	6th	..	..	53.4	39.9	1.8	..	4.9
..	13th	..	..	55.4	35.3	1.6	.3	7.4

TABLE IV.

*Showing the composition of gases from cropped and manured plot.*

Date.				$\frac{\text{o}}{\text{o}} \text{CH}_4$	$\frac{\text{o}}{\text{o}} \text{N}$	$\frac{\text{o}}{\text{o}} \text{CO}_2$	$\frac{\text{o}}{\text{o}} \text{O}$	$\frac{\text{o}}{\text{o}} \text{H}$
August	12th, 1911	..	..	64.4	33.0	1.4	1.2	Nil.
"	26th "	..	..	64.8	24.5	2.5	.8	7.4
September	2nd "	..	..	66.1	15.8	4.9	1.9	11.3
"	9th "	..	..	64.5	21.4	4.1	Nil.	10.0
"	16th "	..	..	52.1	35.5	3.3	1.2	7.9
October	2nd "	..	..	39.7	51.6	6.6	.8	1.3
"	9th "	..	..	21.0	73.7	4.5	.8	Nil.
"	24th "	..	..	18.2	74.7	5.7	Nil.	1.7
"	31st "	..	..	16.6	78.8	4.4	.2	Nil.
November	6th "	..	..	19.5	75.2	4.9	.4	"
"	13th "	..	..	20.4	72.8	4.9	.3	1.6

In these experiments, green-manure to the extent of 8,000 lbs. per acre was puddled in on July 27th, and the fields were again puddled on July 31st and water let in. They were allowed to remain in this condition until August 15th, when the paddy was transplanted. Other than the presence or absence of a crop the two plots were identical in every way and had similar treatment.

A comparison of the results shown in Tables III and IV brings out very clearly the effect of the crop on the composition of the gases, but this is made more apparent in the diagrams on Charts Nos. 3 and 4 where the percentages of Nitrogen and Methane in the gases are plotted in the form of curves. Throughout the whole of the period the percentage of Methane in the gas from the *uncropped* plot was always high and the Nitrogen correspondingly low, whereas in the gas from the *cropped* plot the usual change in composition took place about thirty days after the time of transplanting.

The proportion of Methane falls and that of Nitrogen rises until within six weeks from transplanting their former proportions have been entirely reversed. Another point demanding attention is the behaviour of the crop towards the Hydrogen content of the gases. From the uncropped plot throughout the whole period, and also from the cropped plot up to the time of the change in composition taking place, the gases contained comparatively large proportions of Hydrogen; whereas, after the crop has become fully established

and in strong growth, practically no Hydrogen is present. Thus, besides affecting the relative proportion of Nitrogen and Methane, the crop practically determines the presence or absence of Hydrogen in the soil gases.

The corresponding results for the unmanured plots are given in the following tables:—

TABLE V.

*Showing the composition of the gas derived from the uncropped and unmanured plots.*

Date.				% CH <sub>4</sub>	% N	% CO <sub>2</sub>	% O	% H
August	12th, 1911	..	..	48.4	42.1	1.6	1.6	6.3
"	26th "	..	..	31.5	61.4	1.4	5.7	Nil.
September	2nd "	..	..	57.2	39.9	2.9	Nil.	Nil.
"	9th "	..	..	52.4	43.0	3.9	.7	"
"	16th "	..	..	34.5	62.7	2.1	.7	"
October	2nd "	..	..	33.7	60.9	2.4	3.0	"
"	9th "	..	..	27.3	62.1	5.1	3.4	2.1
"	24th "	..	..	38.5	56.1	2.7	Nil.	2.7
"	31st "	..	..	26.4	66.4	2.6	.3	4.3
November	6th "	..	..	34.4	60.6	2.3	.3	2.4
"	13th "	..	..	32.5	59.2	3.6	Nil.	4.7

TABLE VI.

*Showing the composition of the gas derived from the cropped and unmanured plot.*

Date.				% CH <sub>4</sub>	% N	% CO <sub>2</sub>	% O	% H
August	12th, 1911	..	..	38.7	58.2	1.3	1.2	.6
"	26th "	..	..	Nil.	96.8	3.2	Nil.	Nil.
September	2nd "	..	..	53.8	43.1	2.3	Nil.	.8
"	9th "	..	..	51.6	41.9	2.0	1.4	3.1
October	2nd "	..	..	28.3	68.3	3.2	.2	Nil.
"	9th "	..	..	27.2	67.6	3.7	.6	.9
"	24th "	..	..	12.2	81.5	5.9	.4	Nil.
"	31st "	..	..	17.2	77.5	4.6	.7	Nil.
November	6th "	..	..	20.7	73.2	4.5	Nil.	1.6
"	13th "	..	..	19.2	77.5	3.1	.2	Nil.

In the case of the unmanured plots, it is at once evident that the changes in the composition of the gases are not so marked as in the case of the manured plots, and neither can so much reliance

be placed on the accuracy of the data obtained in the early stage of the experiment, for, the gas production was exceedingly small and samples sufficient for analysis could only be obtained with great difficulty. Further, in many of the earlier samples the gas obtained was obviously present in isolated pockets in the soil, and they could not be looked upon as forming a representative average of the gas present in the plots. Later, as more and more gas accumulated in the soil, representative samples could be obtained and the results in consequence were more reliable. Notwithstanding this, the curves given in Charts Nos. 5 and 6 show that once the crop was thoroughly established small differences in the composition of the gases, analogous to those of manured soils, were present. Thus, in the gas from the uncropped plot, Hydrogen is present in appreciable quantity, but it is practically absent from the gases from the cropped plot. Again after September 16th, the proportion of Methane is lower and that of Nitrogen higher in the gas from the cropped plot than from the uncropped plot. Consequently, these results may be taken as confirming in part the results obtained from the previous experiment, especially when it is remembered that in these unmanured plots no fresh organic matter was added to the soil. The only organic matter present was that constituting the humus of the soil and, this being the residue left from the fermentations of previous years, would be only comparatively slowly attacked. The main fact made clear, however, is that the crop mainly affects the composition of the gases produced from the decomposition of the manure and has little effect on the composition of the gases evolved from the soil organic matter.

A consideration of the foregoing results leads to the conclusions (1) that the gaseous products of the decomposition of organic matter in swamp paddy soils consist chiefly of Methane and a smaller proportion of Nitrogen together with some Carbon-dioxide and Hydrogen; (2) that the introduction of a crop into the soil materially affects the course of the fermentation and results in the production of a gas with a low proportion of Methane, a high one of Nitrogen, and a practically complete inhibition of Hydrogen formation.

CHART NO. 5,

DIAGRAM SHOWING THE VARIATIONS IN THE PERCENTAGE OF NITROGEN  
IN THE GASES FROM CROPPED AND UNCROPPED UNMANURED PLOTS

% NITROGEN IN GAS FROM CROPPED PLOT .....  
" " " " UNCROPPED " \_\_\_\_\_

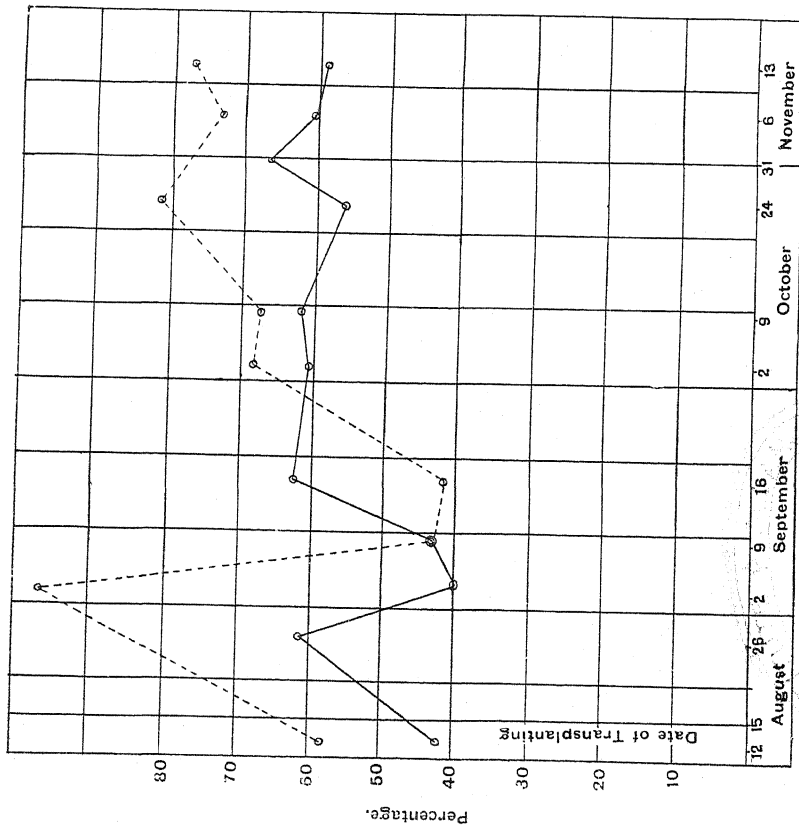
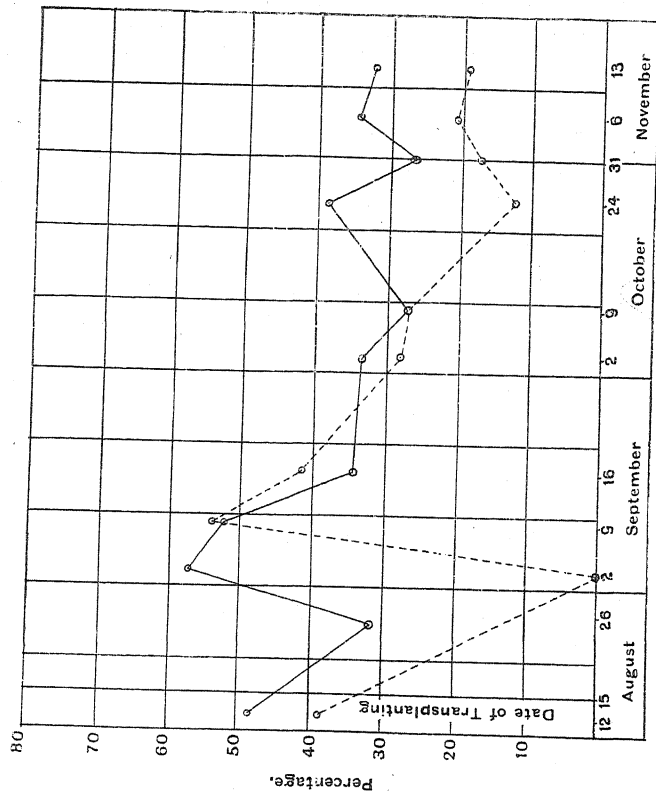


CHART NO 6,

DIAGRAM SHOWING THE VARIATIONS IN THE PERCENTAGE OF METHANE  
IN THE GASES FROM CROPPED AND UNCROPPED UNMANURED PLOTS.

% METHANE IN GAS FROM CROPPED PLOT .....  
" " " " UNCROPPED PLOT \_\_\_\_\_







*The quantity of gas evolved from cropped and uncropped fields.*

Before it is possible to determine the true meaning of the change in composition, it is necessary to obtain relative measurements of the gas production in cropped and uncropped soils. For if less gas is produced in cropped land than in uncropped land, then the production of Methane is being interfered with and possibly that of Nitrogen also. On the other hand, if the gas production is greater in the cropped field, then, under the influence of the crop, Nitrogen is certainly being evolved. Again, if it is assumed that the volume of Methane evolved is the same in both cases, the effect of the crop is to bring about a great disengagement of Nitrogen, whereas, if the volume of Nitrogen is assumed to be the same, the crop prevents the formation of Methane. From whatever standpoint the analytical data are considered, there can be no doubt of the close relationship of the crop with the course of the soil fermentations and the necessity of obtaining some quantitative data becomes of vital importance to a proper understanding of the changes involved.

Unfortunately, this is not so simple a matter as it would appear. The obvious method is to support large funnels over the surface of the soil and to measure and analyse the evolved gases at intervals. When this is done, none of the soil gases are collected but, instead, there appears a gas consisting of entirely Oxygen and Nitrogen, and the volume collected is so great that its main source is obviously from the air or surface water. Under these circumstances, the direct collection of the soil gases by means of inverted funnels fails and recourse must be had, at least in the field, to indirect methods of measurement. This evolution of Oxygen was traced to a film of organized growth spread over the surface of the soil and its relationship to the growth of the plant is considered in the second part of the Memoir.

The usual method employed in these experiments for the collection of the soil gases is capable of giving approximately relative values for the amount of gas accumulated within the soil. On

walking through a field the gas is disturbed and escapes and the amount escaping in a given length will be proportionate to the amount of gas in the soil. Consequently, if the same collecting apparatus is carried the same distance through two fields, the amount collected will be in proportion to the amount of gas in the soils and a relative measurement is obtained.

Applying this method to the cropped and uncropped manured plots previously referred to, the following results are arrived at:—

TABLE VII

*Showing the relative amounts of gas collected in traversing the same distance in cropped and uncropped plots.*

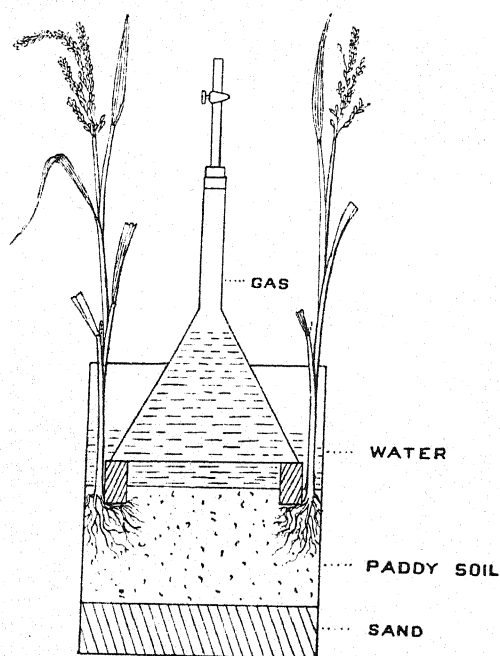
Date.	Ratio. = $\frac{\text{cc. from cropped field}}{\text{cc. from uncropped field.}}$
October 9th, 1911 .	3/2
" 24th " .	11/10
" 31st " .	3/4
November 13th " .	6/5

On the whole these results indicate that the accumulation of gas in cropped land is slightly greater than in uncropped soil. Such rough experiments as these can only be approximate, and it is unwise to draw stringent conclusions from them with reference to the numerical relationship of the volume of gas present in the soil. They can, however, be taken as indications, and justify the conclusion that there is no evidence to show that there is less gas present in the cropped plot; on the other hand, the quantities approximate to equality.

These conclusions apply only to the gases accumulated in the soil but, considering the type and intensity of the fermentation taking place, there must be large quantities of gas escaping through the surface, and the total volume of gas produced, may, in reality, be very dissimilar. The escaping gases are masked and probably profoundly modified in composition through the influence of the surface film previously referred to, and certainly under field condi-

tions no Methane or Carbon-dioxide was detected in the escaping gas. It was found by experiments in pots that this surface film could be prevented from forming by the use of a solution of copper sulphate of the strength of 1 : 250,000, and that when this was done the soil gases passed through the surface of the soil and could be collected and analysed. The strength of copper sulphate used had no detrimental effect on the growth of the crop, and accordingly a series of pot culture experiments were laid down, with the object of measuring the rates of evolution of the gases in cropped and uncropped pots and also of studying the effect of the crop on the composition of the gas.

The pots used were 18 inches deep and 14 inches diameter and had a layer of sand on the bottom 6 inches in thickness. Above this was placed a layer of soil weighing 40 kilos, to which was added green-manure at the rate of 5,000 lbs. per acre. A large inverted funnel 12 inches diameter and with the exit



wood blocks above the soil so that there was a space of half an inch between the rim of the funnel and the soil. The seedlings were arranged in the space between the funnel and the pot, and a depth of water was always maintained in the pot, sufficient to prevent air entering the funnel. The whole arrangement is sketched below.

No drainage was arranged for in these experiments as it was thought advisable to eliminate any conditions which might permit of the copper sulphate entering the soil and so interfering with the course of the

fermentation. In addition, parallel series of unmanured pots were instituted in order to obtain comparisons.

The main difficulty experienced was in preventing the evolution of Oxygen and Nitrogen from traces of the surface film and in fact it cannot be said that this was successfully done with reference to any one pot throughout the whole course of the experiment. When, however, Oxygen was found to be evolved by a pot the addition of copper sulphate at once stopped its further evolution and, as the duplicate pots rarely evolved Oxygen at the same time, it is possible to trace with fair accuracy the rate of evolution of the soil gases.

The gas evolved consisted mainly of Nitrogen with varying amounts of Methane and, for the purposes of comparison, it will be best to consider the latter first, as the contamination arising from the gases evolved from the undestroyed traces of the surface film does not materially affect the results.

The results obtained are tabulated below, and are given up to the date when the grains were fully developed and when the soil would be drained for ripening in the ordinary course of events.

TABLE VIII.

*Showing the Methane production in c.c. from cropped and uncropped manured pots.*

Date.		CROPPED POTS.			UNCROPPED POTS.		
		Pot 1.	Pot 2.	Total.	Pot 3.	Pot 4.	Total.
First period.	8th to 18th January 1913	8.0	1.5	9.5	Nil.	4.2	4.2
	18th to 30th January 1913	6.9	2.1	9.0	2.5	8.4	10.9
	30th January to 12th February 1913	4.4	4.6	9.0	4.0	8.6	12.6
	TOTAL	19.3	8.2	27.5	6.5	21.2	27.7

Seedling transplanted into Cropped Pot on February 13th and the collection of gases recommenced February 24th.



Date.	CROPPED POTS.			UNCROPPED POTS.		
	Pot 1.	Pot 2.	Total.	Pot 3.	Pot 4.	Total.
Second period.	24th February to 7th March 1913 . . .	<i>Nil.</i>	<i>Nil.</i>	<i>Nil.</i>	8.5	8.7
	7th to 19th March 1913 . . .	"	"	<i>Nil.</i>	10.7	10.7
	19th to 29th March 1913. . .	"	"	12.6	13.4	26.0
	29th March to 9th April 1913 . . .	"	"	4.5	10.5	15.0
	9th to 21st April 1913 . . .	"	"	4.7	9.0	13.7
TOTAL		<i>Nil</i>	<i>Nil</i>	30.3	52.3	82.6

The seedlings were not transplanted until February 13th, but before this date the gases were collected from all the pots and in every case Methane was evolved showing that the fermentation was established. After transplanting, Methane continued to be evolved from the uncropped pots, but none was obtained from the cropped ones. This is in entire agreement with the variations in the composition of the soil gases in the field experiments and it is evident that the crop prevents, in some way or other, the normal production of Methane.

During the same period the Methane evolution from the unmanured pots was very small, the uncropped pots only giving  $\frac{1}{7}$  of the volume of the gas evolved from the corresponding manured pots, and at the same time practically no difference could be detected in the evolution from cropped and uncropped unmanured pots. This is in general agreement with the results from the unmanured experimental plots, and it is therefore evident that the Methane evolved from paddy soils is mainly derived from the green-manure and the effect of the crop in altering the composition of the soil gases would, therefore, appear to be due to its relationship to the course of the decomposition of the green-manure. Further, the action of the crop during the growing season is to diminish considerably the production of Methane and Hydrogen.

With regard to the Nitrogen evolution from these pots the results clearly show that much less Nitrogen is evolved from cropped than uncropped pots :—

TABLE IX.

*Showing the total evolution of Nitrogen in c.c. from cropped and uncropped pots from the time of transplanting up to the time of heading (February 24th to April 21st, 1913).*

	Manured.	Unmanured.
Cropped pots . . . . .	220	212
Uncropped pots . . . . .	453	471
Percentage decrease due to crop . . . . .	51%	55%

These results are surprising in many ways. There can, of course, be no doubt as to the effect of the crop in reducing the quantity evolved, but the large production of gas compared to the volume of Methane evolved, and the similarity of the results between the manured and unmanured pots, point strongly to the conclusion that a large proportion of this Nitrogen is not derived from the soil gases.

That its evolution is not due to the action of the surface film is shown on page 95, where the action of copper sulphate in inhibiting the effect of the film is shown, and further support to this view is given by the fact that a manured pot treated with copper sulphate only gave off 105 c.c. of Nitrogen, whereas, a similar untreated pot yielded 445 c.c. from February 24th to April 21st.

Thus, it would appear that there is a surface evolution of nitrogen, unconnected with the soil fermentation or the surface film, due to some undiscovered cause which is affected by the growth of the crop. This being the case, these pot experiments have failed to give any indication of the source of the Nitrogen in the soil and the effect of the crop on the quantity present, but the field measurements throw some light on the problem.

*The source of the Gaseous Nitrogen in the soil.*

The determination of the origin of the soil Nitrogen is of importance and further experiments are being carried out to determine this point with some degree of certainty. This Nitrogen can only come from three sources :—

- (1) The air imprisoned in the soil by the water.
- (2) The Nitrogen dissolved in the irrigation water which penetrates the soil.
- (3) The Nitrogen contained in the organic matter of the soil and manure.

There is no doubt that some of the soil Nitrogen is obtained from the sources indicated in (1) and (2), but a consideration of the amounts of gas obtained from the manured and unmanured plots in the field experiments leads to the conclusion that the larger proportion is derived from the Nitrogen present in the organic manure.

The gases collected by traversing the same distance in each plot were measured and analysed and the relative amounts of Nitrogen obtained are contrasted in the following table in the form of ratios. The ratio between the uncropped *manured* plot and the uncropped *unmanured* plot is referred to as Ratio =  $\frac{UM}{UU}$  and that between the corresponding cropped plots as Ratio =  $\frac{CM}{CU}$ .

TABLE X.

*Showing the relative amounts of Nitrogen present in the manured and unmanured plots.*

Date.						Ratio = $\frac{UM}{UU}$	Ratio = $\frac{CM}{CU}$
October	9th, 1911	.	.	.	.	1.5/1	2.3/1
"	24th "	.	.	.	.	2.6/1	4.3/1
"	31st "	.	.	.	.	3/1	2.6/1
November	6th "	.	.	.	.	1.6/1	2.1/1
"	13th "	.	.	.	.	3.5/1	2.5/1

As the plots contrasted in the above table formed a portion of one small field, they were similar in every respect, with the exception

of the addition of green-manure. Consequently, if the whole of the Nitrogen in the soil came only from the air originally in the soil or from the Nitrogen dissolved in the water draining through it, it would be expected that the ratios would approximate to unity. Instead of this, on the average, about  $2\frac{1}{2}$  times as much gas is present in the manured plots as in the unmanured plots, and the only obvious conclusion is that much of the soil Nitrogen is derived from the manure used and the organic matter present in the soil. This conclusion, taken in conjunction with the fact that less Nitrogen is evolved from cropped pots than uncropped pots, after treatment with the copper sulphate, supports the view that some Nitrogen is absorbed by the plant which otherwise would be evolved as gas in an uncropped field. The evidence is not as clear as we would wish and experiments are being carried out to test the question of this Nitrogen absorption in a more rigorous manner.

*Mode of action of the crop in altering the composition of the Soil Gases.*

It has been shown clearly that the normal evolution of Methane in paddy soil is greatly reduced in amount when a crop is introduced, and there are indications to show that the same probably occurs with the Nitrogen evolution. This being so, a wide field of investigation is opened out to determine the manner in which this action is brought about. It is clear that the crop is the primary cause, but the action may be indirect in the sense that substances may be excreted by the roots which inhibit or retard certain of the phases of the normal fermentation, or it may be direct in the sense that the plant is absorbing some of the decomposition products of the fermentation, thus removing them from the field of action and reducing the intensity of the action by that amount.

With regard to the first possibility, if the effect of the excreted substance were only transitory, it would appear that, when the crop reached full growth, the excretion would be arrested and the course of the normal fermentation re-established, resulting in an increased gas production. Evidence supporting this was obtained in the pot culture experiments for, when the crop reached the

ripening stage such an evolution occurred both with regard to Nitrogen and Methane as is shown in the following table:—

TABLE XI.

*Showing the increased evolution of Gas when the ripening stage is reached.*

Total gas evolution in cc.

DATE.	CROPPED POTS.		UNCROPPED POTS.		REMARKS.
	CH <sub>4</sub> .	N	CH <sub>4</sub> .	N	
9th to 21st April 1913 . . .	Nil.	77.3	13.7	58.4	Ripening stage reached about 21st April.
21st to 28th April 1913 . . .	24.1	52.5	6.6	32.6	
28th April to 5th May 1913 . . .	34.7	34.4	5.3	37.7	
5th to 13th May 1913 . . .	17.3	11.9	3.6	25.6	
Total cc. from 21st April to 13th May 1913 . . . . .	76.1	98.8	15.5	95.9	

Thus once the stage of ripening is reached, we find the cropped pots commencing to evolve Methane in considerable quantities, whereas, previously no Methane was given off. There is also a very large evolution of Nitrogen, and at the same time, the amount of Oxygen present in the evolved gas was very little, only amounting to a few cc., showing the effect of the surface film to be very small. These observations would seem to lead to the view that the effect of the crop is to retard the normal fermentation and some support is given by the behaviour of the unmanured pots. The cropped pots of the latter series showed only a comparatively small increased rate of evolution of Methane and Nitrogen such as would be expected, considering the absence of green-manure and with only the soil organic matter present.

A certain proportion of this evolution of gas in manured pots when the ripening stage is reached may possibly be due to the decomposition of the roots of the crop and not to decomposition of the green-manure recommencing. If this is proved to be the case, the possibility of the changes being due to the absorption by the



roots assumes greater importance. The possibility of the plant absorbing some of the organic compounds produced during certain phases of the fermentation is quite probable in view of the results of recent investigation on the assimilation of organic Nitrogen by the roots of plants. Hutchinson and Miller\* working under sterile conditions have shown that certain plants can utilize the Nitrogen contained in such compounds as acetamide, urea, barbituric acid, alloxan, and to a lesser degree in formamide, glycocoll, oxamide, etc. Schreiner and Skinner† have since experimented with a large number of nitrogenous organic compounds and have come to the conclusion that the plant can absorb them *as such* and that certain of them are utilized by the plant in an advantageous manner, whilst others exert a toxic influence.

Among the substances experimented with by Schreiner and Skinner were many of the compounds produced by the decomposition of proteids and it is just these compounds which would be produced in paddy soils when the green-manure is decomposed. Consequently, if their view is correct, these substances would be absorbed by the paddy roots and the normal fermentation would be lessened in proportion, thus tending to produce a change in the composition of the soil gases.

The whole subject of the relationship of the paddy crop to the soil fermentations is of great importance and is under further investigation.

*The Anaerobic conditions of the soil in relation to Nitrogen assimilation.*

Apart from the question of the relation of the crop to the composition of the soil gases it is evident that the strongly anaerobic conditions prevailing in these swamp paddy soils have a direct bearing on the course of the Nitrogen assimilation of the plant as ordinarily understood. Since Kellner‡ in 1882 showed with swamp

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\* Cent. F. Bakt. 30-513 (1911).

† U. S. A. Department of Agriculture Soil Bureau Bull. No 87, 1912.

‡ Landw. Vers. Station 30 (1884).

paddy that Ammonium salts are more effective as a manure than Nitrates, many investigations have been carried out and the consensus of opinion appears to be strongly against the utility of the latter class of substances, although, possibly with certain varieties of paddy and under certain cultural conditions, Nitrates may be very effective when the plant is heading or approaching ripeness. In recent years Daikuhara and Imasiki,\* in Japan, have shown that denitrification takes place very rapidly in these soils leading to loss of Nitrogen and to the formation of toxic Nitrites. They also showed that Ammonium salts are quite suitable as manures, and that the crop absorbed them as such. Kelly† in Hawaii has confirmed these results and, moreover, showed that Nitrates are not readily absorbed by paddy plants. It may, therefore, be accepted that Nitrates do not persist in these soils, that they are not properly absorbed by the crop, and that poisonous Nitrites are produced from them. Nitrates and Ammonium salts are not used by the South Indian cultivators, but still a knowledge of the behaviour of such substances is of importance, as they are both produced in local soils at one time or another during the season.

These swamp paddy soils are exceedingly clayey in character, and, during the dry season, are fissured in all directions by deep cracks by which air freely enters and thoroughly aerates the soil. Under these conditions nitrification proceeds, and although the crop of weeds, annually raised at this time, must assimilate a great proportion of the produced Nitrates, yet, in the aggregate there must be a considerable quantity of Nitrate present in the soil when the water is admitted for the ensuing paddy crop. The rate at which this Nitrate disappears must depend greatly on circumstances. If the amount of Oxygen imprisoned in the soil is large, or if it persists for some time, or if the fermentation of the green-manure is slow in the earlier stages, this Nitrate may remain undecomposed for some time and have some effect on the crop in the earlier stages just after transplanting.

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\* Bull. Imp. Cent. Agri. Exptl. Stn., Japan, Vol. I, No. 2.

† Bull., 24, Hawaii Agri. Exptl. Stn.

The analysis of the soil gases immediately after water is admitted to the field does not, however, support this view, for on July 27th, 1909, within a very few days after the time of admitting water to the experimental plot, very little gas was present and what there was consisted of 53·4 per cent. Nitrogen, 39·4 per cent. Methane and only ·8 per cent. Oxygen. Further, in 1912, the first samples of gas obtained from the four experimental plots contained from 88·5 to 93·6 per cent. N, 5·8 to 7·1 per cent. CO<sub>2</sub> and only ·6 to 4·4 per cent. Oxygen. Thus it is evident that the anaerobic condition of these soils commences from the date of the first admission of water, long before the crop is introduced into them. Consequently, the Nitrate formed during the dry season is quickly denitrified and is of no value so far as the cultivator is concerned. Neither, in view of the composition of the soil gases and the presence of a large amount of decomposing organic matter in the shape of ploughed-in weeds and green-manure, is the occurrence of nitrification during the growing season probable and the crop must as a consequence derive its necessary Nitrogen from the products of the putrefaction of the proteids present in the green-manure.

It is this aspect of the case which is of importance to the South Indian agriculturalist, and it is one worthy of detailed study. The putrefactive decomposition of green-manure which occurs in these soils leads to the production of a number of substances. The carbohydrates are vigorously attacked under anaerobic conditions and the proteids are decomposed with the formation of albumoses, peptones amine bases, volatile acids of the fatty series, acetic acid, succinic acids, skatol, indol, phenol, ammonia, carbon-dioxide and many other substances. Methane is also produced, according to Omelianski by a special ferment which attacks cellulose, but of which, the authors have discovered no trace in the soils examined. The Ammonia and many of the nitrogenous substances produced are absorbed by the plant and utilized in the formation of tissue and consequently the general suitability of nitrogenous manures for paddy may be stated as follows :—

Manures which contain Ammonia or which yield Ammonia and comparatively simple nitrogenous organic substances on anaerobic decomposition, are suitable manures, whereas Nitrates are not suitable for swamp paddy.

Schreiner and Skinner have shown that not all of these substances are beneficial to the crop. Certain of them appear to be directly assimilated by the crop and are utilized in the formation of tissue, but others have been shown to be toxic and to injure the cropping. Field results in the Tanjore Delta\* show clearly the injurious result which may arise from the application of green-manure to badly drained soils into which young and tender seedlings are transplanted, and there can be no doubt that the beneficial aspect of drainage in relation to swamp paddy soils is partly concerned in the removal of these toxins from the soil. The aspect of drainage to paddy is, however, considered more in detail in the second part of this Memoir.

In localities where the lack of drainage does not permit of the removal of these toxins in the manner indicated, the same end might possibly be achieved by ploughing-in the green-manure several weeks before the time of transplanting, so that some considerable amount of decomposition will have proceeded by the time the young seedlings are introduced. Brieger has observed that the poisonous substances produced during the putrefaction of proteids are only formed in the early stages and that they disappear on prolonged decomposition. It appears therefore probable that the method outlined above would lead to a considerable destruction of the toxins, by the time the seedlings were transplanted.

#### SUMMARY TO PART I.

The conclusions arrived at may be summarized as follows :—

(1) The normal fermentation of green-manure in swamp paddy soils leads to the production of a relatively large proportion of Methane, a smaller amount of Nitrogen, together with some Carbon-dioxide and Hydrogen.

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\* H. C. Sampson's Annual Report of the Manganallur Agri. Station, 1912-13.

(2) The introduction of a crop so modifies the gas production that the proportion of Methane in the gas is greatly reduced and that of Nitrogen increased. The evolution of Hydrogen is practically inhibited.

(3) The action of the crop is to restrict the formation of Methane and Hydrogen either by retarding the rate of fermentation or by a portion of the intermediate products of decomposition being absorbed by the roots. There is also evidence adduced to show that the normal evolution of Nitrogen is retarded in a similar manner.

(4) The soil conditions are shown to be anaerobic in character immediately after water is admitted to the fields, and these conditions persist so long as irrigation proceeds. Under these circumstances, nitrification is impossible and the Nitrates produced during the dry season are quickly denitrified so that the Nitrogen required by the crop is obtained from the Ammonia and nitrogenous organic compounds produced by the anaerobic decomposition of the proteids of the green-manure.

(5) Certain of the substances produced by this decomposition are toxic to the crop, and must be removed in the drainage water, or destroyed by prolonged decomposition before the seedlings are transplanted, otherwise the crop will suffer. The application of green-manure to badly drained areas must, therefore, be undertaken with circumspection and caution.



## PART II.

### *The Gases evolved from the surface of Paddy Soils.*

In the foregoing section of this Memoir attention has been called to the fact that the gases present in the soil itself are dissimilar in composition from the gases which are evolved from the surface of swamp paddy soils. The latter consists mainly of Oxygen and Nitrogen, and we have not been able to detect the presence of Methane, Hydrogen and Carbon-dioxide in them. The last mentioned gases are characteristic constituents of the soil gases and as a consequence there did not appear to be any connection between the soil gases and the surface gases. That there was some relationship, however, between the rate of evolution of Oxygen and the presence or absence of a crop was indicated by a number of haphazard determinations made during the year 1909 and consequently, at the earliest opportunity, some pot-culture experiments were instituted to test this point.

Two pots were taken each 12 inches diameter and 12 inches high with a layer of sand 3 inches deep at the bottom. Over this was placed a layer of paddy soil  $5\frac{1}{2}$  inches thick, thus allowing a depth of  $3\frac{1}{2}$  inches for the surface water. An arrangement for draining the pots was introduced, which consisted of an inverted funnel embedded in the sand layer with its shank connected to a syphon discharging through a tubulure in the bottom of the pot, and the exit of which was closed by means of a rubber tube and pinch-cock. Each pot received green-manure at the rate of 10,000 lbs. to the acre, which was well puddled into the soil, and a certain amount of water was drained off each week, not sufficient, however, to expose the base of the inverted collecting funnels placed above the soil, and so allow air to enter. Paddy was transplanted into one pot on December 21st, 1911, and the other pot remained uncropped.

The gases evolved consisted usually only of oxygen and nitrogen, but in the later stages, a small amount of Methane was sometimes present.

The following table shows the collection of oxygen in cc. :—

TABLE I.

*Showing the rate of collection of Oxygen in cc. from the cropped and uncropped pots.*

DATE.	CROPPED POT.		UNCROPPED POT.		Daily excess of Oxygen given off from the uncropped pot + or -
	cc. O	Daily rate.	cc. O	Daily rate.	
31st December 1911 to 6th January 1912 .	63	10.5	204	34.0	+23.5
6th to 12th January 1912 .	130	21.6	241	40.0	+18.4
12th „ 19th „ „ .	191	27.2	234	33.4	+6.2
19th „ 26th „ „ .	244	34.9	183	26.1	-8.8
26th January to 7th February 1912 .	315	28.6	542	49.2	+20.6
7th to 21st February 1912 .	584	41.7	738	52.7	+11.0
21st February to 5th March 1912 .	568	43.7	833	64.0	+20.3
Total and average .	2,095	average 32.2	2,975	average 45.7	average +13.5

It is evident that in this experiment the effect of the crop was to lessen the evolution of Oxygen by 880 cc. or equal to 13.5 cc. per day on the average. It is also evident that the absorption of Oxygen is not uniform throughout the period, but that it took place in two stages. A reference to the last column of the table will show this, where the daily excess of Oxygen evolved from the uncropped pot is given. From December 31st to January 19th the daily excess gradually diminishes until, between January 19th and February 7th, there is more Oxygen evolved from the cropped than the uncropped pot. Afterwards there is an excess of Oxygen evolved from the uncropped up to the end of the experiment.

These results were so definite that it was decided to lay down a more extensive series of experiments and, accordingly, two series were started early in 1913. The two series were parallel experiments and differed from each other only in the depth of the pots

and the size of the collecting funnel. Each series consisted of cropped and uncropped manured pots and similar unmanured pots.

In Series I the pots were 18 inches high and 14 inches diameter with a layer of sand 6 inches thick on the bottom and above this 40 kilos of soil. The gas collecting funnel was 10 inches diameter. Series II consisted of pots 16 inches high and 12 inches diameter with a 6 inches layer of sand and 20 kilos of soil. The funnel in this case was only 8 inches diameter. To the manured pots green-manure was added at the rate of 5,000 lbs. per acre.

All the pots were undrained, thus differing from the previous experiment. The seedlings were introduced on February 12th, but the gases were not collected until the seedlings were established on February 24th.

The results are tabulated below :—

TABLE II.

*Showing the Oxygen evolution from the pots of Series I.*

Date.	MANURED POTS.					UNMANURED POTS.				
	CROPPED.		UNCROPPED.		Daily excess of Oxygen from cropped pots + or —	CROPPED.		UNCROPPED.		Daily excess of Oxygen from cropped pots + or —
	cc. O	Daily rate cc.	cc. O	Daily rate cc.		cc. O	Daily rate cc.	cc. O	Daily rate cc.	
24th Feby. to 3rd March 1913 . .	2.3	.33	2.4	.34	+ .01	14.9	2.12	1.5	.21	—1.91
3rd March to 10th March 1913 . .	2.4	.34	26.3	3.75	+3.41	14.8	2.11	2.0	.28	—1.83
10th March to 17th March 1913 . .	9.1	1.30	56.4	8.05	+6.75	1.9	.27	15.4	2.20	+1.93
17th March to 28th March 1913 . .	14.9	1.35	65.5	5.95	+4.60	1.2	.24	43.1	3.91	+3.67
28th March to 4th April 1913 . .	13.5	1.92	31.2	4.45	+2.53	1.4	.20	28.0	4.00	+3.80
4th to 11th April 1913 . .	20.0	2.85	23.1	3.30	+ .45	1.5	.21	38.6	5.51	+5.30
11th to 17th April 1913 . .	15.3	2.55	26.7	4.45	+1.90	.7	.10	30.4	5.06	+4.96
17th to 23rd April 1913 . .	16.3	2.71	44.4	7.40	+4.69	1.1	.18	19.9	3.31	+3.13
23rd to 30th April 1913 . .	51.2	7.31	17.3	2.47	—4.84	2.4	.34	12.8	1.82	+1.48
30th April to 7th May 1913 . .	54.3	7.75	29.3	4.18	—3.57	11.4	1.62	7.7	1.10	—1.52
Total and average	199.3	2.76	322.6	4.48	+1.72	51.3	.74	199.4	2.77	+2.03

TABLE III.

*Showing Oxygen evolution from the pots in Series II.*

Date.	MANURED POTS.					UNMANURED POTS.				
	CROPPED.		UNCROPPED.		Daily excess of oxygen from uncropped pot + or —	CROPPED.		UNCROPPED.		Daily excess of oxygen from uncropped pot + or —
	cc. O	Daily rate cc.	cc. O	Daily rate cc.		cc. O	Daily rate cc.	cc. O	Daily rate cc.	
24th Feby. to 3rd March 1913	3.2	.47	61.2	8.74	+ 8.27	5.4	.77	7.8	1.11	+ .34
3rd to 10th March 1913	2.6	.37	43.5	6.21	+ 5.84	1.5	.21	18.9	2.70	+ 2.49
10th to 17th March 1913	1.2	.17	63.3	9.04	+ 8.87	2.0	.28	39.8	5.68	+ 5.40
17th to 28th March 1913	1.1	.10	107.4	9.76	+ 9.60	.5	.04	125.3	11.39	+ 11.35
28th March to 4th April 1913	5.1	.72	45.5	6.50	+ 5.78	.4	.05	39.0	5.57	+ 5.52
4th to 11th April 1913	6.9	.98	75.6	10.80	+ 9.82	1.1	.15	65.2	9.31	+ 9.16
11th to 17th April 1913	7.0	1.16	68.2	11.36	+ 10.20	3.1	.52	59.0	9.83	+ 9.31
17th to 23rd April 1913	3.4	.56	48.6	8.10	+ 7.54	10.1	1.68	31.7	5.28	+ 3.60
23rd to 30th April 1913	3.8	.54	35.7	5.10	+ 4.56	9.2	1.31	22.8	3.25	+ 1.94
30th April to 7th May 1913	3.5	.50	25.2	3.60	+ 3.10	7.6	1.08	27.0	3.85	+ 2.77
Total and average	37.9	Average, .52	574.2	Average, 7.97	Average, + 7.45	40.9	Average, .56	436.5	Average, 6.06	Average, + 5.50

These results, like those of the earlier experiment, show a much less evolution of Oxygen from the cropped pots than from the uncropped ones. The smaller evolution of Oxygen from the cropped pots only continues during the active growing period, for, as soon as the ripening stage is reached (about April 23rd) an increased evolution occurs, and in fact, in the first series more Oxygen is evolved than from the corresponding uncropped pots.

The difference between the rates of evolution of cropped and uncropped pots is shown in the above table and this may be looked upon as measuring an absorption of Oxygen by the crop. With the exception of the unmanured pots of Series No. I there is a sudden decrease in the rate of absorption about the first week of April, just before the crop headed and it would, therefore, appear as if the

growth of paddy took place in two stages. What bearing this has on manurial and cultural problems is not quite clear; but it is interesting to note that around Palghat, it is customary, on certain types of soil, to manure the crop at half growth. The authors are under the impression that a similar procedure is customary with certain Chinese cultivators of paddy.

The smaller evolution of Oxygen from the cropped pots and its relation to the stage of growth of the plant implied some connection between the life of the crop and the production of Oxygen at the surface of the soil. At this stage our colleague Dr. C. A. Barber very generously placed before us the results of his examination of paddy roots of different types which led him to the conclusion that these roots are not typical water plant roots, as would be expected, but that they are similar to the roots of ordinary dry land crops and, as such, they would require aeration if their healthiness is to be maintained. It was, therefore, concluded that the Oxygen evolved at the surface of the soil was utilized by the plant for the purpose of aeration of the roots.

The cause of this evolution was traced by us to a film of organized growth spread over the surface of the soil which varies considerably in character in different localities. Algæ of various kinds are usually present in considerable quantity, but occasionally films are obtained which are practically devoid of such growths. Diatoms are invariably present, occasionally to such an extent as to produce a friable white skin over the surface of the dried off soil, which has been mistaken for a saline incrustation. Apart from these organisms, there appears to be a constituent of the film of a bacterial nature. During the progress of the pot culture experiments a film grew up the interior of the funnels, which was slightly brown in colour, due to the presence of diatoms and earthy particles, but which contained no green algæ. Under the microscope it was found to consist of irregular filaments which show no definite structure and which are covered with bacteria, the latter being arranged with their long axis parallel to the direction of the filament. Occasionally films are obtained from the fields which



contain a very small proportion of algal growth and which appear to consist almost entirely of this unorganized filamentous growth together with diatoms.

In Plate II, Fig. 1 shows the general character of this film and Fig. 2 a single filament magnified 1,000 diameters.

The function of this latter growth is at present undetermined. Considering the facts that (1) we have not been able in the field to demonstrate the presence of gaseous Carbon compounds in the surface gases, and (2) the amount of Oxygen evolved from a field is increased by the presence of green-manure in the soil (page 104), it would appear possible that this growth brings about a change in the carbon constituents of the soil gases such as to make them available as food for the green algæ. Support is given to this by the fact that we have been able to isolate cellulose, or some closely related substance, from films which contained no green algæ or organised growths other than diatoms.

These observations, which led us to the conclusion that the aeration of the roots is largely due to the agency of the surface film, practically supplement and confirm the work of Brizi,\* in Italy, work to which our attention has only recently been called. Brizi states that the roots of the rice plant do not conform to the aquatic type and showed, by means of water cultures, that aeration was absolutely essential for their growth. He also showed that the introduction of algæ, obtained from rice fields, into cultures devoid of Oxygen, but in which Carbon-dioxide was present, was sufficient to thoroughly aerate the roots and promote healthy growth. This was due to the algæ assimilating the Carbon-dioxide and liberating Oxygen. His experiments led him to the conclusion that the presence of algæ in rice fields must largely increase the quantity of dissolved Oxygen in the irrigation water and lead to the efficient aeration of the roots. His work, taken in conjunction with our measurements, shows clearly the importance of the surface growth to the crop. In the best examples of this surface film, it is

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\* *Annuario Dell' Istituzione Agraria* Dott. A. Ponti, Vols. V, VI and VII, 1905-06 and '08.

PLATE II.

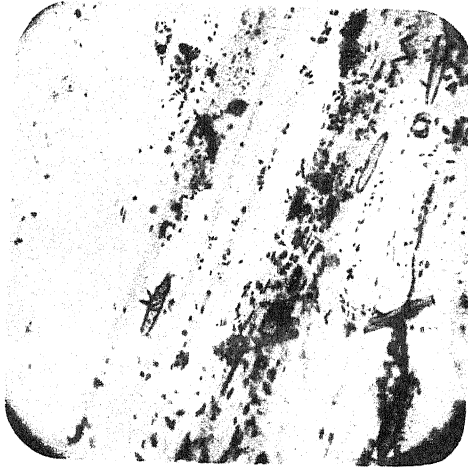


Fig. 1



Fig. 2



thick and tenacious and practically continuous over the surface of the field. Between it and the soil surface accumulate large bubbles of gas which on analysis rarely contained less than 50 per cent. Oxygen, so that under normal conditions there is an atmosphere very rich in Oxygen in contact with the soil and capable of strongly aerating any water passing into the soil or water already present in the soil and in contact with the Oxygen.

Reference has been made to the fact that the surface gases evolved from paddy soils consist not only of Oxygen, but contain large quantities of Nitrogen as well, and the connection between the two is shown by the fact that applications of copper sulphate greatly reduce the evolution of Nitrogen just in the same way that the Oxygen evolution is inhibited. This is well shown in the following table which gives the results from a typical experiment.

TABLE IV.

*Showing effect of Copper sulphate in inhibiting the evolution of the Surface Gases.*

DATE.	cc. O.	Daily rate in cc.	cc. N.	Daily rate in cc.	REMARKS.
23rd December 1912 to 3rd January 1913	13.6	1.23	19.8	1.80	No copper sulphate present.
3rd to 7th January 1913 . . .	7.6	1.90	21.4	5.35	
7th to 18th January 1913 . . .	.5	.05	5.5	.55	
18th to 30th January 1913 . . .	.9	.07	9.0	.75	Copper sulphate present.
30th January to 12th February 1913 .	1.2	.09	9.6	.73	

It would appear that this Nitrogen is derived originally from the air and that its evolution is obviously connected with the presence or absence of a surface film. The analysis of the gases from cropped and uncropped pots also brings out clearly the fact that the amount of Nitrogen evolved depends upon the presence or absence of a crop and varies approximately with the amount of Oxygen evolved from any one pot. The cropped pots give off less Nitrogen than the uncropped pots, and the difference between the volumes

shows in a general way the same variations as those of the Oxygen evolution.

The evolution of Nitrogen would, therefore, appear to be dependent upon that of Oxygen, thus pointing to its being a purely physical phenomenon. The Oxygen evolved is the residue of the Oxygen produced by the surface film which has escaped absorption by the roots and collects, as we have shown, in bubbles under the film. The green algal growths give off practically pure Oxygen, so that, in the first instance, bubbles of pure Oxygen will collect. Surrounding these bubbles is water containing amounts of Oxygen and Nitrogen in solution proportionate to their partial pressures in the atmosphere, but at the point of contact with the bubble the partial pressure of Oxygen becomes relatively high and that of Nitrogen low; consequently there is a tendency for Oxygen from the bubble to go into solution and nitrogen to come from the water to its place. This action will go on until equilibrium occurs and the bubble of gas will no longer consist of pure Oxygen but a mixture of the two gases.

The greater the amount of Oxygen collecting at the surface of the soil the greater will be the quantity of Nitrogen evolved. Thus the rate of the Nitrogen evolution from the pots will follow generally that for the Oxygen.

*The effect of the Drainage and Aeration of the soil on the crop.*

On considering carefully the results of our observations on the relationship of the evolution of Oxygen to the aeration of the roots, it was clear to us that the drainage of paddy soils must be an important factor with regard to the amount of aeration produced in them. In undrained soils the aerated water at the surface of the soil could not possibly enter the soil and consequently, aeration would be restricted to the surface layers of soil. On the other hand, drainage would cause the aerated surface water to penetrate into the soil and aeration would be deeper. This being so it appeared probable that the depth of aeration would be proportionate to the



rate of drainage, and the greater the rate of drainage the deeper would be the aeration of the soil with, probably, a proportionately increased cropping.

Again, as the aeration of the roots bears such an important relationship to the growth of the crop it appeared to us probable that the effectual aeration of the soil could be achieved with the expenditure of much less irrigation water than normal, by periodically draining the pots completely and thus permitting air to enter the soil. Further, this aeration of the soil would produce more aerobic conditions and there would be less danger of an excessive amount of toxic substances being produced. The conditions would also be more suitable for nitrification and this might have a favourable action on the growth.

Accordingly to test these points two separate experiments were instituted, one series to determine the effect of varying rates of drainage on the cropping, and the other to test the effect of aerating the soil by permitting the pots to drain thoroughly between consecutive irrigations.

#### *The effect of Drainage on the crop.*

In this experiment the pots were 12 inches in diameter and contained, on the bottom, a layer of sand weighing 10 kilos and above this a layer of 12 kilos of soil. 40 grammes of green-manure were added to each pot and drainage was provided for by means of an inverted funnel filled with sand, embedded in the sand layer and connected to a syphon discharging through the tubulure in the base of the pot. Continuous drainage was not given, but each pot, on the appointed date, was allowed to drain until the surface soil was nearly uncovered when the drainage was closed and fresh water added. The time elapsing between consecutive drainings varied from 1 to 7 days, but each pot received uniform treatment throughout the experiment. When the time of ripening approached, all the pots were drained and only kept moist until the harvest was taken. The same number of plants were present in each pot.

The results obtained are given in the following tables :—

TABLE V.  
*Showing the Grain Production.*

EXPERIMENT.	SERIES I.			SERIES II.		
	Wt. of grain in gms.	Loss or increase.	Wt. of N. in gms.	Wt. of grain in gms.	Loss or increase.	Wt. of N. in gms.
Undrained . . . . .	11.15	..	.094	12.15	..	.113
Drained every 7th day . . . . .	13.47	+2.32	.107	13.80	+1.75	.121
.. .. 3rd .. . . .	14.45	+3.30	.127	17.65	+5.50	.147
.. .. 2nd .. . . .	11.92	+ .77	.117	14.25	+2.10	.139
.. .. day . . . . .	12.08	+ .93	.108	13.60	+1.45	.132

So far as the production of grain is concerned, it is at once evident that drainage exerts an exceedingly beneficial effect. At the same time, it is apparent that this effect is not in proportion to the amount of drainage, but that a maximum effect is produced with only a moderate amount. Excessive drainage reduces the yield to within measurable limits of the undrained pot. The amount of Nitrogen accumulated in the grain also shows the same variations.

TABLE VI.  
*Showing Straw and Chaff Production.*

EXPERIMENT.	SERIES I.			SERIES II.		
	Wt. in gms.	Loss or increase.	Wt. of N. in gms.	Wt. in gms.	Loss or increase.	Wt. of N. in gms.
Undrained . . . . .	24.70	..	.079	21.45	..	.072
Drained every 7th day . . . . .	19.75	—4.95	.065	21.80	+ .35	.071
.. .. 3rd .. . . .	26.40	+1.70	.104	27.45	+6.00	.091
.. .. 2nd .. . . .	20.57	—4.13	.067	26.10	+4.65	.092
.. .. day . . . . .	24.37	— .33	.099	26.00	+4.55	.060

Although the agreement between these two series is not good, yet, it is evident that the maximum production of straw is produced with drainage every 3rd day.

Consequently, it would appear that paddy requires only a moderate amount of drainage to enable the crop to produce its maximum yield, too much drainage being detrimental.

*The effect of Aerating the Soil.*

The pots in these experiments were 12 inches diameter and 17 inches high. 12 kilos of sand were placed on the bottom and over this a layer of 15 kilos of earth and drainage was arranged for as described in the previous experiment. 40 grammes of green-manure were puddled into the soil of each pot.

One pot remained undrained throughout the whole period and of the remaining pots a system of alternate swamping and draining was instituted. All the pots were allowed to remain covered with water for three days and then were allowed to drain for 1, 2, 4 or 8 days before being swamped again. The drainage was complete in each case, thus causing air to enter the soil, the object being to induce conditions more likely to cause nitrification than those normal to swamp soils and also to endeavour to obtain a relative measure of the values of dissolved Oxygen and gaseous Oxygen in aerating the roots.

The results are set forth in the following tables:—

TABLE VII.

*Showing the effect of different periods of Soil Aeration on the Production of Grain.*

EXPERIMENT.	SERIES I.			SERIES II.		
	Weight of grain.	Loss or increase.	Weight of Nitrogen.	Weight of grain.	Loss or increase.	Weight of Nitrogen.
Un aerated	14.58	..	.145	14.48	..	.147
Covered for 3 days and drained 1 day	16.30	+1.72	.175	15.89	+1.41	.164
Covered for 3 days and drained 2 days	16.60	+2.02	.186	14.36	— .12	.151
Covered for 3 days and drained 4 days	12.76	—1.82	.136	10.57	—3.91	.102
Covered for 3 days and drained 8 days	5.38	—9.20	.066	4.65	—9.83	.054

Thus, aeration of the soil has an effect which reaches a maximum at between one and two days' aeration, yielding on the average about a 10 per cent. increase, but longer aeration than this is very detrimental and the yields are much worse than those of the un-aerated pot.

TABLE VIII.

*Showing the effect of different periods of Aeration on the Production of Straw and Chaff.*

EXPERIMENT.	SERIES I.			SERIES II.		
	Weight of straw.	Loss or increase.	Weight of Nitrogen.	Weight of straw.	Loss or increase.	Weight of Nitrogen.
Un-aerated	24.07	..	.081	22.82	..	.077
Covered for 3 days and drained 1 day	29.78	+5.71	.106	27.94	+5.12	.093
Covered for 3 days and drained 2 days	31.20	+7.13	.107	25.98	+3.16	.088
Covered for 3 days and drained 4 days	23.84	—23	.105	20.88	—1.94	.088
Covered for 3 days and drained 8 days	12.97	—11.10	.056	12.62	—10.20	.068

The production of straw follows the same variations as that of grain, but in a more distinct manner as the maximum increase is about 20 per cent.

The conclusion is evident that a small amount of aeration leads to a somewhat heavier cropping, but the increase obtained, so far as grain is concerned, is not so marked as with simple drainage. It would therefore seem that the admission of air to the soil does not lead to as effective aeration as simple drainage. The explanation of this would appear to lie with the concentration of the dissolved Oxygen in the soil water. We have previously shown that the normal condition of paddy soils is such that the water entering the soil is very strongly aerated owing to its having been in contact with an atmosphere very rich in Oxygen, whereas the admission of air into the soil would yield a weaker solution approximately equal to that produced by contact with air and the aeration of the

roots would be proportionately less. The further conclusion may also be drawn that Oxygen to be effective must be presented to paddy roots in a state of solution.

One fact was very clear that the periods of aeration, if prolonged much over 24 hours, had the effect of preventing the formation of the surface film and thus the aeration of the roots during the period of swamping was not effective.

*The effect of Drainage on the Root action of Paddy.*

The action of moderate amounts of drainage in promoting increased cropping is obviously connected with the introduction of a greater amount of dissolved Oxygen into the soil. An examination of the root development in the drained and undrained pots showed that this increased aeration had led to a deeper and more extended root action. In the undrained pots the greater proportion of roots were distributed through the top layer of the soil at the point where aeration could only take place and consequently, the mass of soil from which they drew their substance, was restricted and the crop suffered as a consequence. On the other hand, in the drained pots the penetration of Oxygenated water into the depths of the soil had induced a deeper root development. This action of drainage is well shown in the photographs in Plates III & IV where the root development in undrained and drained pots is contrasted. Although, with a small amount of drainage there is a much deeper root development than in the undrained condition, yet, there does not appear to be a greater production of roots, for, the undrained pots yielded a total of 19.75 grammes of dried roots and the pots drained every third day 19.90 grammes. On the other hand, a quick rate of drainage reduces the amount of root produced, the pots drained every day only yielding 11.7 grammes.

These results of the drainage experiment are apparently conflicting. It would be expected that increased drainage would lead to increased aeration, by bringing larger volumes of aerated water in contact with the roots. Whereas, the maximum effect is

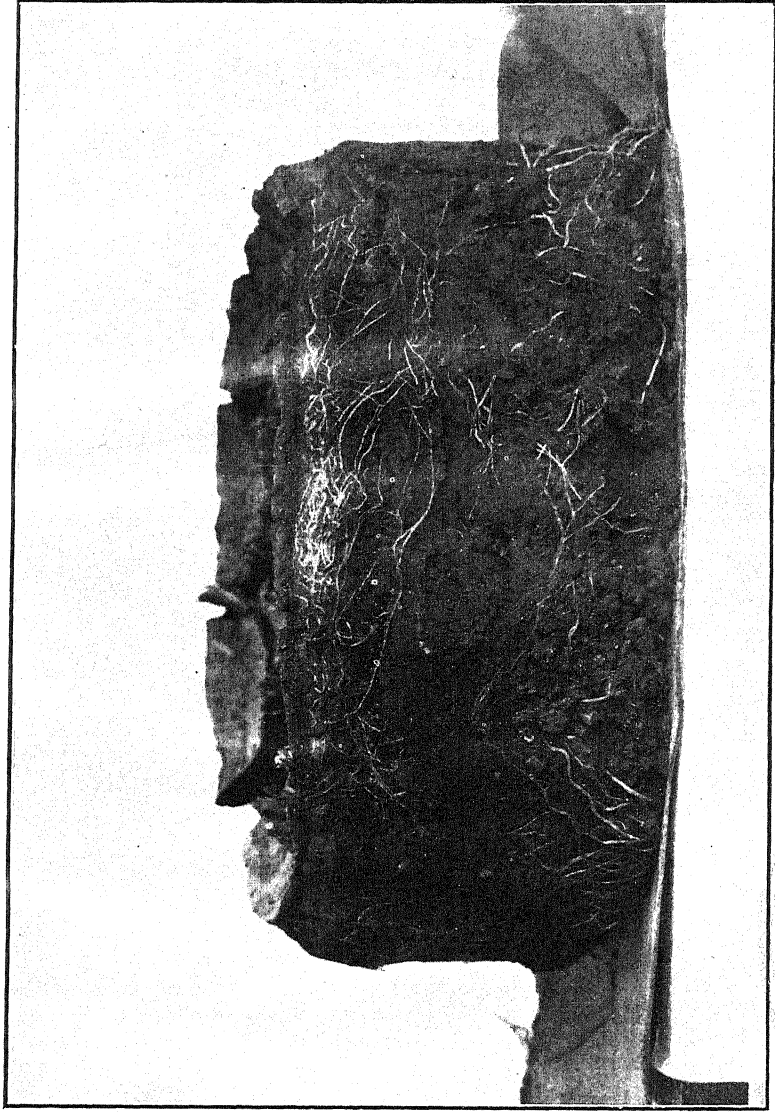
attained with a comparatively slow rate of drainage, and increased rates lead to reduced cropping and root development. The explanation lies in the fact that the quicker rates of drainage had the effect of decreasing the growth of the surface film and, as a matter of fact, no visible film formed in the pots drained every day. It is, therefore, apparent that quick drainage, by inhibiting the growth of the surface film and thus preventing the evolution of Oxygen at the surface of the soil, may actually lead to decreased aeration of the roots. *Thus, the most efficient rate of drainage is not the quickest, but that one which permits the film to maintain full activity.*

This being the case, the explanation of the universal custom of puddling these soils and so reducing the drainage through them is apparent. During the dry season the soils dry and shrink and their physical condition becomes coarser so that their rates of drainage would be increased. On puddling the soils when water is admitted the aggregate particles formed during the dry period are broken down and the soil returns to its original condition and rate of drainage. It is obvious that the amount of puddling given will affect the drainage in proportion and it would therefore appear that the ryot has at his command a simple method of regulating the latter, and as a consequence, the aeration of his soils.

The relation of drainage to aeration has also an important bearing on the formation of new paddy soil. Dry soils, even when of a heavy nature, do not yield their maximum crop of paddy at once when converted into wet lands. Usually, the yields of the first few years are exceedingly poor and it is only after several years have elapsed that such land is looked upon as even fair swamp paddy soil. Some investigations carried out by us several years ago led us to the conclusion that, in the first few years after paddy cultivation is initiated on land previously under dry cultivation, the main change taking place was a sorting of the particles between the soil and sub-soil, the coarser particles tending to accumulate in the sub-soil and *vice versa*. Afterwards, this action diminished and then it is

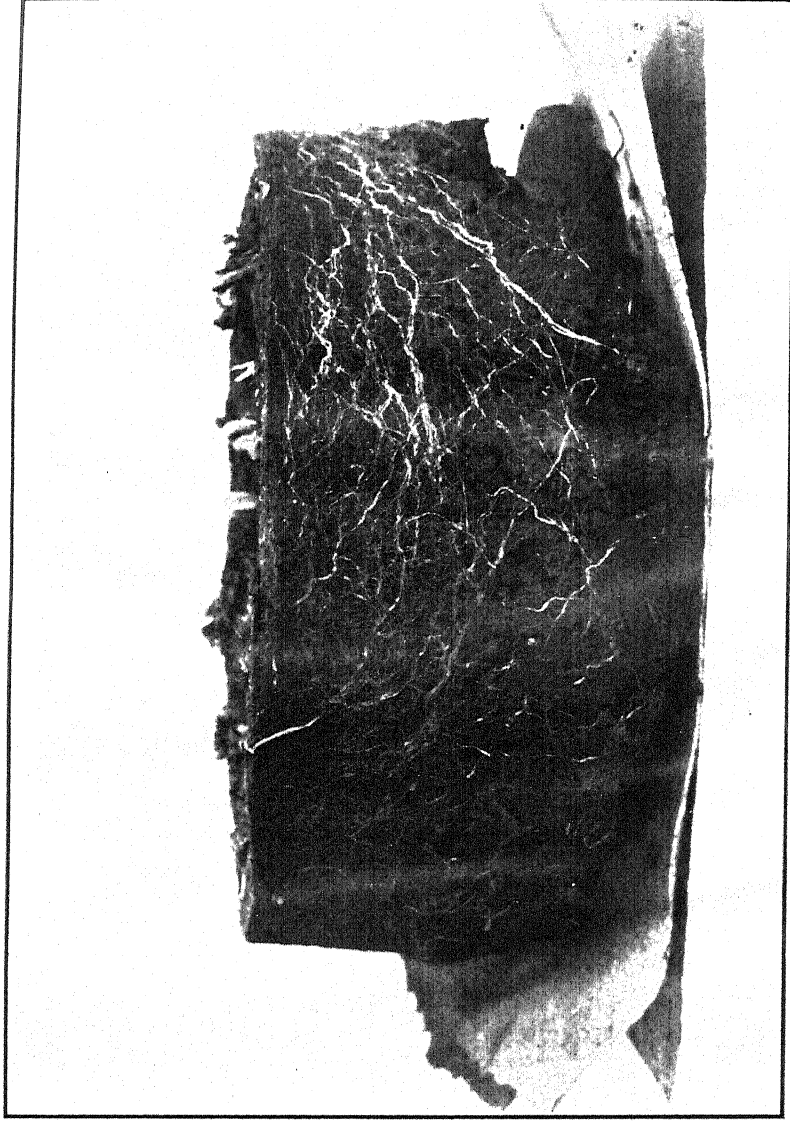


PLATE III.



Root Development in *undrained* pot.

PLATE IV.



Root Development in *drained* pot.

possible to demonstrate that, in both soil and sub-soil, the main effect of the cultivation is a breaking down of the soil particles, thus producing a heavier soil as years go on. Thus in these new soils the rate of drainage is continually tending to diminish and it is not until this rate permits the formation of the surface film that the maximum yields are obtained.

Hutchinson\* has recently published an article dealing with relationship of drainage to rice soils showing that drainage is beneficial to the cropping which he ascribes to the removal by the drainage water of the toxins produced by the decomposing manure, and also to the possibility of the formation of Nitrates. There can be no doubt that one of the functions of drainage is the removal of noxious substances from the sphere of the activity of the roots, as we have pointed out in Part I, but we are unable to agree to his theory of Nitrate production.

In the first place, if the good effects of drainage were merely due to the removal of toxins and the formation of nitrates from the Oxygen dissolved in the water then, within reasonable limits, the quicker the drainage the better should be the results obtained. In our experiments the removal of water every second day cannot be looked upon as constituting an excessive rate of drainage, yet the results in cropping were very much worse than those produced by a slower rate of drainage.

Further the relation of Nitrates to well drained paddy soils has been studied by Kelly† in Hawaii who has shown that (1) denitrification is very rapid, (2) if Nitrates are present, poisonous Nitrites are produced and a concentration of the latter of only 5 parts per million of soil injures the crop, (3) rice seedlings are unable to assimilate Nitrates, and (4) Nitrates used as a manure show little or no effect and, in pot culture, stunt the growth. The evidence adduced

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\* Agri. J. India, Vol. VIII, Part 1, page 35. 1913.

† Loc. cit.

by Kelly goes to show that the formation of Nitrates in swamp paddy soils would not help the plant.

In addition, when it is taken into consideration that in our field experiments we only found traces of Oxygen in the soil gases, the possibility of Nitrate formation is very remote, especially in the presence of large quantities of decomposing green-manure. The drainage of the fields experimented with was quite good so far as paddy soils go.

The results of our aeration experiment would also appear to support the contention that Nitrates are not utilized by the plant, for, with admission of air to the soil, the fermentation of the green-manure would become more aerobic in character and the formation of toxic bodies reduced in amount, and, at the same time, the conditions would be more favourable to the production of Nitrates. The results, although showing some improvement with a slight amount of aeration, are not so good as those produced by simple drainage and in fact strong aeration leads to a decreased outturn.

*The relationship of Green-manuring to the aeration  
of the Roots.*

From the point of view of the South Indian cultivator the relationship of the green-manure, which he uses, to the aeration of the roots is of prime importance. Does the presence of this large quantity of organic matter in the soil tend to prevent efficient aeration of the roots or does it improve the aeration by increasing the activity of the surface film?

In a previous paragraph we have discussed the relationship of the film to those constituents of the soil gases which contain Carbon and we have indicated the possibility that these substances are intercepted by the film and are utilized in such a way as to promote increased activity. If this is the case, it would be expected that the increased fermentation going on in the soil owing to the presence of

green-manure would lead to a greater production of Oxygen by the film. That this is the case is shown in the following table :—

TABLE IX.

*Showing the production in cc. of Oxygen and Nitrogen in manured and unmanured uncropped pots from December 23rd, 1912, to May 13th, 1913.*

	SERIES I.		SERIES II.	
	Oxygen cc.	Nitrogen cc.	Oxygen cc.	Nitrogen cc.
Amount evolved from manured pots . . .	577	1,134	952	983
"    "    "    unmanured pots . . .	391	702	634	788
Increased " evolution due to manure in per cent. . . . .	47%	61%	50%	24%

Thus the evolution of Oxygen was increased on the average by 48 per cent. in the presence of green-manure and that this extra gas was utilized by the crop is shown in the following table :—

TABLE X.

*Showing amount of Oxygen in cc. absorbed by manured and unmanured crops from February 24th, 1913, to April 23rd, 1913.*

	SERIES I.		SERIES II.	
	Manured.	Un-manured	Manured.	Un-manured.
Oxygen evolved from cropped pots—cc. . .	93·8	37·7	31·6	22·7
"    "    "    uncropped pots—cc. . .	276·0	180·2	523·3	391·1
Difference indicating the amount absorbed by crop . . . . .	182·2	142·5	491·7	368·4

In both series there is more Oxygen absorbed by the manured crop than by the unmanured crop to an extent, on the average, of 31 per cent. Consequently, not only does the addition of green-manure to a soil lead to an increased evolution of Oxygen, but this increased amount is available and is utilized by the crop. Thus, apart from all considerations of manurial value or its function in altering the physical texture of the soil *one of the most important*

*functions of green-manuring lies in promoting an increased activity of the surface film which leads to greater aeration of the roots.*

The practice of green-manuring, so general in South India, is, therefore, quite sound in principle so long as there is drainage present in the soil. It is only when the drainage is deficient that the toxins produced during the fermentations are able to affect the growth of the crop detrimentally, and under these conditions, the green-manuring should only be undertaken after careful consideration and even then with great circumspection.

#### SUMMARY TO PART II.

These investigations have led the authors to the conclusion that the surface film of algæ, etc., which covers the surface of swamp paddy soils and which evolves large quantities of Oxygen, is the chief agent in causing the aeration of the roots of the crop.

The Oxygen evolved by this film is dissolved in the irrigation water and thus produces a very highly aerated solution from which the roots derive the Oxygen essential for them. In undrained soils, this solution does not penetrate into the soil, and, consequently, the roots are congested near the surface of the soil and the amount of soil from which they derive their food is therefore limited and the crop suffers. In drained soils this strongly aerated water penetrates the soil and the roots are able to penetrate to a greater depth. The mass of soil from which the food supply is drawn is increased and the crop benefits in proportion.

Too great a rate of drainage decreases the formation of the film and the aeration of the roots is thereby lessened. There is therefore for all swamp paddy soils an optimum rate of drainage which produces the greatest aeration and this rate of drainage is a comparatively slow one.

Aeration of these soils by atmospheric Oxygen is not as effective in promoting root aeration as is aeration by the water draining through them.

The use of green-manures in drained paddy soils induces a greater activity on the part of the surface film, thus leading to a better aeration of the roots.



## PREFACE.

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In publishing the following account of tests of the error which occurs when taking a sample of sugar-cane from a field or plot, I desire to express my indebtedness to Dr. Gilbert T. Walker, C.S.I., F.R.S., for valuable suggestions as to the best mode of solving the problem, and to Mr. Gordon Canning, of the Parsa Factory, for rendering facilities when sampling his fields of sugar-cane.

AGRICULTURAL RESEARCH  
INSTITUTE, PUSA,  
*May, 1913.*

}

J. W. L.





## THE EXPERIMENTAL ERROR IN SAMPLING SUGAR-CANE.

By

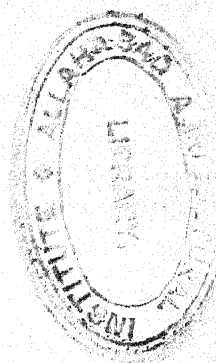
DR. J. WALTER LEATHER, V.D., PH.D., F.I.C.,

*Imperial Agricultural Chemist.*

DURING the last four years tests have been made of the error which is involved when taking a sample from a plot or field of sugar-cane. It is generally known that, however "pure" and uniformly cultivated a plot of cane may be, all the canes, even among those which are apparently equally ripe, will not be alike, that variations occur among the canes and that consequently it is not sufficient to take some one cane as representing the whole, but that a number must be taken as a "sample." The question which is involved is then a perfectly definite one, namely, "how many canes must be taken and in what manner should these be selected from the field or plot?"

Speaking quite generally, when a "sample" of any material, whether this is a crop in the field, or the harvested produce, or raw or manufactured article, is taken, the object in view is to select a small portion of the whole in such a way that the "sample" will represent the whole as perfectly as possible. This small portion or sample may then be examined by one means or another and the quality of the whole judged by the quality of the sample.

Sometimes the material is homogeneous. For example, pure salt or pure saltpetre may be manufactured, or a liquid such as alcohol mixed with water prepared. In such case one portion of the whole will be of necessity precisely like any other, and hence



any small portion will truly represent the whole. In such a case no error is involved when taking the sample.

Agricultural produce and manufactured articles generally are not homogeneous and for this reason one portion is not exactly like another portion. In fact, whilst in the case of homogeneous substances any two samples must be *necessarily* alike, in the case of heterogeneous (*i.e.*, non-homogeneous substances) no two samples will be exactly alike; this fact is very generally acknowledged. There is then among samples of agricultural produce an *error*. The sample is taken to represent the whole; no two samples are alike; and hence it is clear that since there is a divergence between the samples, no such sample can truly represent the whole; the difference between the quality of the sample and that of the whole is the error attaching to the sample.

The subject of taking a sample portion of a commodity is not a new one, but until comparatively recent years the best mode of doing so has depended on the fancy of the person who is interested. Latterly the subject has been examined mathematically with the aid of the theory of probabilities,\* so that "fancy" and "rule of thumb" may now be replaced by a more dependable "system."

In connection with agricultural work generally, the probability formulæ have been very usefully applied in recent years,† and important deductions regarding the error which is involved, not only in taking a sample but also in respect of field and feeding experiments, have been made. Thus it has been shown that quite small plots of  $1/40$  or  $1/50$  of an acre are for many purposes as accurate as those measuring  $1/4$  or  $1/2$  acre; that in feeding experiments not less than 30 animals should be included in each lot; that in order to value a root crop sufficiently well,

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\* See E. G. Bailey, *J. Ind. & Eng. Chem.*, I (1909), 161; M. L. Griffen, *J. Soc. Chem. Ind.*, XXVIII (1909), 192; and S. H. Collins, *Proc. Univ. of Durham Phil. Soc.*, 1908-9, p. 129.

† Wood & Stratton, *J. Agri. Sci.*, III, p. 433; also four papers published as Supplement No. 7, *Jour. Bd. Agri.*, November 1911.

about 100 roots must be taken to make a sample. The subject is particularly clearly dealt with in the first of the papers mentioned, namely, that by Wood and Stratton.

It is not appropriate to enter here into an exhaustive explanation of the theory of probabilities. The subject is very lucidly explained in text-books.\* It is perhaps best put to the agricultural reader thus. Supposing good pure seed of a particular variety of any crop is sown, the plants produced will in no case be all precisely alike, in fact, it is highly *probable* that no two of them will be alike. It is well here to emphasise the word "probable," because the case just taken illustrates the necessity of bearing in mind that we are dealing with probabilities and not with certainties. What is meant is simply that whilst some two of the plants *may* be alike, it is very highly probable that *all* will be different from one another. At the same time, given good seed of a pure strain, it will be found on a careful examination of each of the plants that a large proportion of them will be very much alike, whilst a smaller number will differ from the majority to a greater extent.

#### SUGAR-CANE.

What has been said in the last section about the variability in crops applies naturally to sugar-cane and it was merely necessary to decide on what method to make the tests and to carry these out, in order to arrive at a solution or partial solution of the question which had been proposed, namely, how a sample of sugar-cane should be taken. The question arises very frequently. The factory in India does not purchase cane according to quality, but in some cases at least the manufacturers are very anxious to know what the general or average quality of different varieties is. These come to the factory so mixed that a fair sample of any one variety cannot readily be taken there. If, however, a depend-

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\* For example, "A Text-Book on the Method of Least Squares" by Mansfield Merriman. Pub., J. Wiley & Sons. "The Theory of Errors and Method of Least Squares" by W. W. Johnson. Pub., J. Wiley & Sons. "Higher Mathematics" by J. W. Mellor. Pub., Longmans Green & Co

able sample can be taken readily from a field, the quality of the cane could be ascertained. Again, there is the agriculturist who wishes to compare several varieties which he may grow side by side or he may wish to compare these with the same grown by cultivators, or he may wish to test the same variety grown by ryots in different villages—possibly on different soils. There is, too, the sugar specialist who may be growing from individual canes or from seed. To him the *individual* variation among canes must be of great importance as well as the average quality. In all events the same two questions really occur, namely, what is the individual variation, and what is the variation over a certain area, for without a knowledge of these variations one cannot decide how to sample the crop.

During the first two seasons at Pusa, numbers of small groups of cane, such as three, six, or twelve canes in the group were tested, and from these the quantity of cane which would be required from a certain area was estimated. The result of this when compared with samples which had been taken on a quite different plan at Partabgarh, went to show what the probable error was in different cases, as also that the Partabgarh samples had been probably larger than was necessary. The result was, however, not altogether satisfactory and the work was at Dr. Walker's suggestion continued in 1913 on different lines.

It was assumed that the variation among canes might be attributed generally to two primary causes, (a) that due to the "plant" and (b) that due to "soil." It is to be understood that under these two terms are included *all* causes of variation, and hence either of them includes several factors. For example, the several canes of any one stool will not be all of the same age or the same degree of maturity or of the same size; such factors will naturally all be causes of variation; these and any others appertaining to the plant are included in the first named group of causes. Similarly under the separate head "soil," are included actually all other causes of variation such as accidental differences in cultivation, spacing, manuring and the like. In



fact it was merely thought that by so differentiating causes of variation the solution of the problem would be simplified. As the sequel shows, it seems probable that such a separation of the several factors is not possible.

It was assumed that in any one case the field or plot contained only one variety of cane, and whilst there is some evidence that this was not strictly true in all cases, the mixture such as it has been seems to have been very uniform.

In order to ascertain the variation (a) due to "plant," it was assumed that if a number of canes were taken from a quite small area, the effect of the second factor (b) "soil" would be negligibly small. Accordingly the mode of operating was as follows:—(a) From *one place* in the plot successive canes were cut roughly in concentric rings and analysed separately; as many as 120 individual canes were thus dealt with in any one case at Pusa. From the test of these the variation exhibited by individual canes was calculated. With this information it was possible to form an idea of the number of canes which would be required in order to reduce the error of the mean to within certain limits. (b) If then this latter number of canes were taken from all over the plot, the error of the mean was expected to increase, the increase in error being due to the "soil." If this latter variation were considerably greater than that due to the "plant," it would be demonstrated by the increased probable error over that which was found under section (a). The work proved to be very considerable and in fact only three plots were tested at Pusa and four plots at a factory in the north of Behar, but it has resulted in a very clear indication of what the variation among canes is and what size of sample is desirable from a plot or field.

#### VARIATION AMONG INDIVIDUAL CANES.

In order to ascertain the variation among individual canes, one cane after another was cut from a plot, the cutting starting from a centre and continuing from this concentrically. All canes were taken excepting (a) those young shoots which would not be harvested by a cane grower, and (b) those which were obviously

so diseased as to be worthless. The former exception will be readily admitted. Regarding the diseased canes opinions will differ. Some might argue that no diseased cane should be included in this class of work. If diseased cane were readily detected by the eye, the argument might be allowed. Such ready detection of disease is, however, far from being the case. Canes may have either fungus in them or an insect borer without showing it at least readily, and the greater part of any one cane may be quite sound. In any case the damage can often only be detected by splitting the cane throughout its length. Again, both at Pusa and at the Parsa Factory a very high proportion of the canes were diseased to a limited extent. It may be held that if such canes were included, a greater variation would be found than among entirely sound canes, and thus indicate the necessity of taking a larger sample of cane from a field than might in good sound cane be actually necessary; such an error would, however, be preferable to the reverse. Another objection to the separation of canes which *might* appear to be diseased would be that personal bias would come into play. *It is most important* in such work as this that the sample shall be taken as *mechanically* as possible; any picking and choosing would only lead to wrong deductions.

The canes were numbered as they were cut, and the following determinations carried out:—

(i) Each cane was weighed, crushed, and the weight of juice recorded.

(ii) The juice was clarified and the sucrose determined by direct polarisation.

(iii) The glucose was determined in as many samples as was possible in the time available.

From each of three varieties growing at Pusa, 120 canes were thus tested and the data regarding the sucrose in these are set out in Statements Nos. I, II, III (*vide* pages 113—115 of this memoir). It has been decided to publish these in detail because so little information of this nature is available in sugar-cane literature.

## STATEMENT No. I.

*% Sucrose in juice of individual canes. Chinia variety.  
Pusa, 1913.*

Cane No.	Sucrose. %	Cane No.	Sucrose. %	Cane No.	Sucrose. %
1	14.9	41	14.9	81	15.1
2	14.5	42	17.6	82	10.5
3	15.6	43	17.0	83	15.9
4	16.2	44	11.3	84	12.3
5	16.0	45	12.8	85	13.5
6	15.1	46	16.2	86	9.5
7	15.6	47	11.6	87	11.9
8	16.4	48	13.3	88	9.3
9	15.5	49	17.0	89	13.2
10	13.3	50	15.3	90	11.9
11	15.7	51	12.4	91	3.4
12	14.2	52	15.2	92	6.9
13	15.1	53	11.8	93	14.4
14	17.3	54	13.9	94	7.6
15	14.9	55	12.5	95	6.4
16	13.0	56	16.8	96	11.9
17	13.2	57	9.5	97	8.1
18	14.2	58	13.4	98	9.7
19	15.3	59	8.7	99	14.1
20	15.8	60	13.4	100	16.2
21	12.0	61	14.6	101	14.8
22	10.4	62	13.9	102	11.9
23	10.7	63	12.6	103	14.7
24	10.1	64	12.1	104	16.3
25	10.1	65	13.5	105	14.4
26	13.9	66	14.3	106	13.6
27	15.7	67	13.5	107	17.3
28	13.8	68	10.3	108	15.4
29	13.9	69	9.2	109	17.4
30	14.1	70	12.8	110	11.3
31	16.1	71	15.8	111	13.2
32	15.2	72	10.4	112	10.9
33	16.7	73	13.0	113	12.4
34	15.8	74	8.9	114	12.5
35	16.4	75	13.6	115	13.7
36	16.5	76	16.9	116	15.4
37	16.3	77	14.6	117	9.8
38	15.2	78	3.6	118	9.3
39	15.9	79	11.1	119	13.1
40	15.9	80	11.9	120	6.6

## STATEMENT No. II.

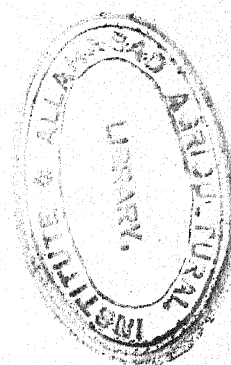
% Sucrose in juice of individual canes. *Mungo variety.*  
*Pusa, 1913.*

Cane No.	Sucrose. %	Cane No.	Sucrose. %	Cane No.	Sucrose. %
2	16.8	41	12.2	81	17.9
3	18.2	42	10.0	82	16.9
4	10.7	43	9.9	83	15.8
5	13.8	44	14.1	84	6.5
6	11.5	45	15.3	85	13.1
7	18.7	46	15.7	86	15.1
8	18.2	47	16.9	87	14.0
9	18.3	48	14.1	88	16.2
10	14.6	49	13.2	89	15.3
11	21.4	50	14.0	90	17.8
12	19.5	51	12.3	91	11.5
13	7.9	52	14.4	92	10.1
14	14.5	53	13.1	93	18.0
15	17.5	54	18.0	94	16.0
16	16.1	55	18.7	95	16.1
17	17.5	56	16.9	96	10.5
18	13.8	57	18.0	97	10.5
19	17.9	58	18.0	98	12.5
20	13.5	59	12.5	99	12.7
21	14.7	60	15.6	100	14.0
22	16.9	61	15.1	101	16.7
23	14.4	62	17.5	102	14.1
24	16.3	63	16.5	103	17.1
25	17.7	64	10.7	104	17.1
26	16.5	65	12.5	105	18.5
27	17.6	66	18.7	106	17.3
28	17.9	67	19.3	107	19.5
29	16.7	68	20.3	108	7.6
30	14.4	69	14.0	109	19.0
31	14.4	70	15.4	110	15.0
32	10.2	71	15.9	111	14.4
33	13.2	72	13.6	112	13.8
34	13.8	73	15.1	113	14.2
35	15.0	74	12.3	114	11.0
36	15.2	75	14.4	115	11.4
37	13.8	76	14.4	116	16.2
38	18.2	77	14.9	117	16.3
39	18.9	78	16.2	118	18.6
40	17.3	79	19.0	119	18.7
	15.0	80	15.8	120	18.5

## STATEMENT No. III.

*% Sucrose in juice of individual canes. Khari variety.  
Pusa, 1913.*

Cane No.	Sucrose. %	Cane No.	Sucrose. %	Cane No.	Sucrose. %
1	13.8	41	16.3	81	17.6
2	14.5	42	14.9	82	17.5
3	12.6	43	14.6	83	16.8
4	15.4	44	17.5	84	16.0
5	17.0	45	18.1	85	16.3
6	17.0	46	17.2	86	16.3
7	16.7	47	16.2	87	16.7
8	17.5	48	16.9	88	16.0
9	16.8	49	14.9	89	16.9
10	15.9	50	15.1	90	10.2
11	15.2	51	15.4	91	17.3
12	13.3	52	16.6	92	10.0
13	17.5	53	16.7	93	17.3
14	16.9	54	18.1	94	9.9
15	13.8	55	17.4	95	14.5
16	15.1	56	15.6	96	14.1
17	11.2	57	17.3	97	13.9
18	15.6	58	17.3	98	14.1
19	16.2	59	17.9	99	13.8
20	15.9	60	14.0	100	16.4
21	15.9	61	17.1	101	15.8
22	17.1	62	17.7	102	14.8
23	17.6	63	16.3	103	8.8
24	10.8	64	18.1	104	13.1
25	16.7	65	18.0	105	15.4
26	16.9	66	18.8	106	15.4
27	17.1	67	17.8	107	17.6
28	17.1	68	14.6	108	13.0
29	16.2	69	16.7	109	12.5
30	3.2	70	17.2	110	17.1
31	16.7	71	13.4	111	17.5
32	17.4	72	15.7	112	15.1
33	15.8	73	13.7	113	14.3
34	17.1	74	16.9	114	15.7
35	17.6	75	12.0	115	17.7
36	17.9	76	16.5	116	16.6
37	17.7	77	16.5	117	17.8
38	16.8	78	17.6	118	16.3
39	17.6	79	17.7	119	13.3
40	1.6	80	16.1	120	10.8



## STATEMENT IV.

*% Sucrose in juice of individual canes—Parsa, 1913.*

STRIPED TANA.		KHARI.		BHURLI.		EKRI.	
Cane No.	Sucrose. %	Cane No.	Sucrose. %	Cane No.	Sucrose. %	Cane No.	Sucrose. %
1	16.5	1	14.0	1	21.9	1	14.2
2	15.7	2	12.5	2	20.8	2	12.1
3	16.8	3	13.3	3	13.1	3	14.5
4	16.6	4	15.4	4	20.7	4	11.7
5	15.8	5	17.0	5	20.9	5	11.5
6	14.5	6	6.2	6	20.0	6	12.4
7	18.1	7	16.3	7	22.1	7	16.4
8	18.1	8	10.5	8	13.5	8	13.8
9	17.4	9	10.5	9	19.7	9	11.4
10	18.3	10	15.8	10	21.3	10	13.2
11	19.4	11	15.7	11	22.0	11	12.5
12	17.9	12	14.8	12	20.6	12	13.9
13	17.6	13	16.1	13	20.6	13	12.6
14	17.0	14	14.4	14	8.8	14	11.8
15	16.9	15	12.0	15	17.8	15	9.9
16	17.8	16	13.5	16	20.6	16	14.6
17	18.4	17	12.0	17	20.6	17	12.7
18	17.3	18	13.8	18	19.1	18	10.6
19	19.8	19	18.2	19	12.3	19	11.1
20	14.4	20	15.0	20	19.7	20	11.2
21	18.3	21	17.2	21	19.3	21	14.0
22	17.0	22	16.1	22	21.6	22	11.2
23	17.5	23	13.7	23	19.2	23	12.2
24	18.1	24	10.5	24	14.1	24	13.2
25	17.3	25	14.6	25	10.2	25	12.9
26	17.2	26	16.5	26	9.3	26	13.8
27	17.6	27	6.9	27	21.4	27	12.1
28	14.1	28	16.0	28	18.0	28	12.5
29	11.9	29	13.3	29	22.4	29	12.3
30	14.4	30	17.0	30	22.2	30	12.9
31	17.5	31	18.5	31	20.7	31	13.1
32	18.3	32	18.0	32	19.4	32	14.4
33	15.9	33	17.2	33	20.0	33	10.9
34	15.2	34	14.6	34	19.4	34	14.7
35	11.8	35	15.4	35	20.0	35	12.7
36	17.6	36	16.3	36	20.1	36	12.8
37	19.2	37	5.0	37	17.8	37	13.3
38	18.1	38	15.4	38	19.1	38	12.6
39	18.7	39	15.4	39	18.4	39	11.4
40	15.0	40		40	19.4	40	15.9

From these data the probable error  $r$  of the individual and the probable error of the mean  $r_0$  have been calculated. These are tabulated in the subjoined statement No. V.



## STATEMENT No. V.

Variety.		JUICE.			SUCROSE.			GLUCOSE.		
		$\gamma$ .	Mean %	$\gamma^{\circ}$ .	$\gamma$ .	Mean %	$\gamma^{\circ}$ .	$\gamma$ .	Mean %	$\gamma^{\circ}$ .
Chinaia	...	$\pm 2.80$	68.6	$\pm .26$	$\pm 1.92$	12.35	$\pm .17$	$\pm .294$	1.25	$\pm .040$
Mungo	..	$\pm 4.18$	65.3	$\pm .38$	$\pm 1.92$	15.17	$\pm .17$	$\pm .317$	.73	$\pm .044$
Khari	...	$\pm 3.24$	63.4	$\pm .30$	$\pm 1.53$	15.58	$\pm .14$	$\pm .101$	.27	$\pm .014$

In order to estimate the value of these tests it is best to compare the number of canes of each variety which proved to come within the limits of  $M \pm r$ . For this purpose the percentage of sucrose is taken.

## STATEMENT No. VI.

STATION.				VARIETY.	NUMBER OF CANES WITHIN LIMITS $M \pm r$	
					Found.	Expected.
Pusa	...	...	...	China.	61	60
Do.	...	...	...	Mungo.	58	60
Do.	...	...	...	Khari.	65	60

It is evident from these comparisons that there was not only a large variation among individual canes, but also that the number examined was not quite sufficient to admit of the numbers agreeing well with the laws of probability.

After testing these varieties at Pusa and completing the corresponding tests on the larger plots of the same cane which are described subsequently, the investigation was transferred to the Parsa Factory, for it was obviously desirable to bring into the comparison the variations among canes growing under other conditions and where possibly disease would be less severe than at Pusa. It was, however, only necessary to ascertain whether the variation at Parsa was markedly different from that at Pusa, because if the difference proved to be only slight, the Pusa data

would be substantiated. Hence, and also because testing large numbers of canes is very tedious, only 40 individual canes of each variety were tested at Parsa. Moreover the mills available were much less reliable than that at Pusa and the record of percentage of juice was consequently of little value. The glucose could not be determined. The results are set out in the statements Nos. IV and VII.

STATEMENT No. VII.

VARIETY.	SUCROSE.		
	<i>r</i>	Mean %.	<i>r</i> <sub>o</sub>
Striped Tana ...	$\pm 1.18$	16.88	$\pm 19$
Khari ...	$\pm 1.81$	14.19	$\pm 29$
Bhurli ...	$\pm 2.19$	18.70	$\pm 35$
Ekri ...	$\pm .92$	12.76	$\pm 14$

The numbers of canes which fell between the limits were as follows :—

STATEMENT No. VIII.

VARIETY.	NUMBER OF CANES WITHIN LIMITS $M \pm r$ .	
	Found.	Expected.
Striped Tana ...	21	20
Khari ...	16	20
Bhurli ...	24	20
Ekri ...	18	20

The individual variation was therefore so far as one can tell from these small numbers quite as great at Parsa as it had been at Pusa.

To this however may be added the following comparison of analyses of individual canes.\* In the chapter on Sugar-cane, van der Stok quotes the results of analyses of individual canes from plots of two sorts, which had grown very uniformly.

\* Die Züchtung der landwirtschaftlichen Kulturpflanzen. C. Fruwirth, Vol. V, p. 18.

## Variety No. 228—

% Sucrose	...	7-8,	8-9,	9-10,	10-11,	11-12.
No. of canes	...	18	55	99	58	20

## Variety No. 247—

% Sucrose	...	4-5,	5-6,	6-7,	7-8,	8-9,	9-10,	10-11,	11-12,	12-13,	13-14.
No. of canes...	10	16	18	25	30	64	33	26	17	11	

The exact percentage of each is not given, but on the assumption that it was midway between the limits in each case, the following values for the individual variation have been calculated:—

Variety No. 228,	$+ \cdot 64,$
Do. 247,	$+ 1 \cdot 55.$

Another example may be quoted from Wood and Stratton's paper.\* In the series of tests of the amount of dry matter in 160 individual mangold roots Wood and Berry found the value of  $r$  to be  $\pm 1 \cdot 1$ —

No. of roots within the limits  $M \pm r$

Found	Expected
81	80

In this series the correspondence between the numbers found and expected is much closer than that found for the Pusa sugar-canes; a result which is in part attributable to a larger number having been tested, but also no doubt to the greater uniformity in the quality of the crop. It is thus seen that considerable variation among individual plants is to be expected and that the variation among the canes at Pusa and at Parsa was not really an abnormal one. Kobus† also found the individual variation among the canes of a stool to be so great that he considered it necessary to test the whole in order to obtain a reliable mean value.

\* Jour Agri. Sci., III.

† Int. Sugar Jour., Nos. 90 and 91 (1906); Sugar-cane by Noel Deerr, p. 125.

## VARIATION DUE TO SOIL.

Having obtained the foregoing information as to individual variation, it was decided to proceed with tests of the variation due to "soil." But here a departure from the original intention was practically necessitated. This had been to take from all over the plot, in as well distributed a manner as possible, such a number of canes as would reduce the error due to "plant" to very small limits. It had been intended to take three or four times the number which the work on the individual variation indicated. The individual variation had shown that with 120 canes the probable error of the *mean* was  $r_o = \pm 17$  in two cases and  $\pm 14$  in the third. This error had proved to be in fact a great deal larger than was hoped would be the case. If the error due to "soil" should prove to be considerable, then a number of times this many canes must be taken in order to determine its value.

Taking large numbers of canes, especially from the thinner varieties, such as those which were at our disposal, is not a simple case of walking down the rows as it would be for example in a root crop, and cutting the canes as required; it is, on the other hand, a time absorbing matter because of the interlaced condition of the canes, and it became evident that in order to arrive at results quickly, an attempt must be made to limit the work.

Consideration was therefore given to the question "what error is probable in any simple method of sampling." With a probable error of  $r_o = \pm 17$ , the following are the expectations:—

Error $r_o$	Probability
$\pm 17$	1 : 1
$\pm 34$	4 : 1
$\pm 51$	95 : 5
$\pm 68$	993 : 7

Thus the variation due to "plant" was such that if only 120 canes were taken as a sample, the true value of the whole might

be expected to be wrong by more than .5 per cent. sucrose in one case or sample in 20.

It is a question for the experimenter to decide for himself within what limits of accuracy he wishes to ascertain the mean value of his plot of cane, but with the experience which had been gained at Pusa over three seasons, and at Partabgarh, as well as with the West Indian canes, it appeared probable that a much higher degree of accuracy than  $\pm 5\%$  of sucrose would be difficult to secure.

With these various considerations in mind, it was decided to test in the first place the value of a sample of about 200 canes in each case taken over the whole of a plot, *and to depend on duplicate samples* to show the probable error. The value of duplicate samples in such a case as the present is only considerable when a number of such tests is made. For example, supposing duplicate samples from the first plot had been taken and it had been found that these were very similar, that is, that the difference between them was only quite small, it would not have been admissible to argue that this was sufficient for our purpose, because agreement between duplicates in an isolated case might readily be accidental. The value of the difference between duplicates only rises when the number of such duplicates is great enough to yield a dependable mean value for the differences. Given, however, a sufficient number of such duplicates, they form the most reliable test of the error in sampling. This error is naturally due to *all* causes of variation, which have been classed as (a) due to "plant" and (b) due to "soil." By the tests of 120 canes the error due to (a) had been, it was thought, approximately ascertained; hence it was expected that the error, now to be measured by a series of duplicate samples, would be greater because all causes of error, both "plant" and "soil," were included in it. These samples were not always taken on the same day or by the same assistant, but they were always taken from different places in the crop. The increase in number of canes from 120 to 200 would not, so far as probabilities are concerned, reduce the error due to individuality

very much because the probable error is expected to vary inversely as the square root of the number of canes; in fact, it would have but little effect on the result if the number actually taken were 150 or 250 canes, but it would act as a security that the value of the error due to the "plant" would not be greater when these were taken from over the whole area than it had been found in the one spot.

It is now necessary to mention one factor which is very essential when taking these canes. It has been pointed out that there must be no "picking and choosing." The canes must be taken as mechanically as possible. If the individual canes were well spaced, as for example in a root crop, there would be no difficulty. It would be merely necessary to decide that  $x$  canes are to be taken from area  $A$ , at uniform intervals; the number from each row, taken at specified intervals in the row, could be stated, and those canes situated at the specified positions cut out. But on measuring from the end of a row of cane to a specified distance along the row, there is usually found not one cane, but several canes all approximately equally near to the specified point, and it would be open to the person who is sampling the cane to *select* a certain cane. Now it is just this *selection* which must be avoided if a true result is to be obtained. Consequently it was decided this year, as also in preceding years at Pusa, that this difficulty could only be overcome by taking not one but several canes from any specified point. Thus on laying down the measuring chain or tape at the required point, his orders were to cut (in 1913) those three canes which came nearest to the measured point. These might belong to one stool or to two. In some cases only a single cane, in others only two canes would occur near the point in question, in which case these were taken; or in some cases there was found no cane for several feet distance, in which case no cane was to be taken. It may be thought that it would often happen that the three canes would come from the one stool and that among these the variation would be materially less than among canes from different stools. This may be so, but the evidence provided by the tests of



individuality indicates that this is not the case. Since it was laid down to take *about* 200 canes in lots of three, it followed that the sampler had to take three canes from about 70 places. These were to be as evenly distributed over the plot as could be conveniently arranged. Hence for an approximately square plot the number of rows was divided by 8 or 9, and 9 or 8 lots of three canes each taken from approximately equidistant points in each of the specified rows. In case the plot was not square, the distribution of the points from which to cut out the cane was made to suit the dimensions.

Commencing with an area of  $\frac{1}{10}$  acre in two of the varieties and taking two such samples in each case, it was found that the probable error of any one sample was not greater, but actually less than that found from the tests of individual canes, that is, the error due to "soil" variation seemed to be negligibly small on at least this area. Next duplicate samples were taken from  $\frac{1}{8}$  or  $\frac{1}{4}$  acre of the same varieties, when again the probable error of the sample was found to be not greater than that due to individuality. Finally the area was increased to 1 acre when a like result was met with.

With this experience from Pusa to guide one, it was decided to sample 1 acre at Parsa where this was possible; in one case the whole area of the plot was only  $\frac{1}{4}$  acre.

The results thus obtained at Pusa and at Parsa may now be tabulated.

STATEMENT No. IX.  
*The results obtained from duplicate samples.*

Variety.	Area acre.	Number of canes taken for each sample.	Juice. Mean % <i>r</i>	Sucrose. Mean % <i>r</i>	Glucose. Mean % <i>r</i>
China (Pusa) ...	$\frac{1}{10}$ {	$\begin{matrix} 151 \\ 129 \end{matrix}$ }	$67.45 \pm .90$	$11.55 \pm .660$	$1.35 \pm .012$
Ditto ...	$\frac{1}{3}$ {	$\begin{matrix} 347 \\ 353 \end{matrix}$ }	$66.6 \pm 1.31$	$10.40 \pm .018$	$1.45 \pm .012$
Ditto ...	1 {	$\begin{matrix} 186 \\ 168 \end{matrix}$ }	$65.9 \pm .36$	$11.0 \pm .120$	$1.40 \pm \text{nil}$
Mungo (Pusa) ...	$\frac{1}{10}$ {	$\begin{matrix} 215 \\ 216 \end{matrix}$ }	$55.8 \pm .84$	$13.77 \pm .030$	$1.04 \pm .042$
Ditto ...	$\frac{1}{3}$ {	$\begin{matrix} 188 \\ 189 \end{matrix}$ }	$58.1 \pm .84$	$12.75 \pm .179$	$.94 \pm .018$
Khari (Pusa) ...	$\frac{1}{10}$ {	$\begin{matrix} 202 \\ 184 \end{matrix}$ }	$65.21 \pm .61$	$13.34 \pm .036$	$.76 \pm .018$
Ditto ...	$\frac{1}{3}$ {	$\begin{matrix} 235 \\ 230 \end{matrix}$ }	$66.70 \pm .24$	$12.01 \pm .191$	$1.36 \pm .119$
Ditto ...	1 {	$\begin{matrix} 214 \\ 215 \end{matrix}$ }	$64.25 \pm .90$	$12.96 \pm .137$	$1.20 \pm .143$
Khari (Parsa) ...	1 {	$\begin{matrix} 212 \\ 216 \end{matrix}$ }	.....	$13.38 \pm .155$	.....
Bhurli (Parsa) ...	1 {	$\begin{matrix} 210 \\ 210 \end{matrix}$ }	.....	$20.64 \pm .114$	.....
Ekri (Parsa) ...	1 {	$\begin{matrix} 205 \\ 204 \end{matrix}$ }	.....	$13.50 \pm .173$	.....
Bansgira (Parsa) ...	$\frac{1}{3}$ {	$\begin{matrix} 186 \\ 180 \end{matrix}$ }	.....	$16.61 \pm .179$	.....

The probable error, *r*, is that derived from duplicate samples, and corresponds in a measure with the probable error of the mean  $r_0$  of the individual canes; not rigidly because the latter was not "weighted" with the weight of cane or the percentage of juice, but no large mistake will be made by a general comparison. If then the values under "sucrose  $r_0$ " of Statement No. V are compared with those of "sucrose *r*" of Statement No. IX it will be seen that the latter are generally the smaller though there is no marked distinction.

THE PROBABLE ERROR OF A SINGLE MEASURE.

From the differences obtained between the duplicate samples, the probable error of a single determination of sucrose

over any area up to 1 acre may be calculated from the equation \*

$$r = \pm .4769 \sqrt{\frac{\Sigma p d^2}{n}}$$

The value of  $p$ , the weight of any pair of determinations, might for all practical purposes be taken as unity. But in order to weight the tests, and especially since a majority of the percentages of sucrose are comparatively low, the unit 15 per cent. sucrose has been assumed and the following obtained, the effect of area being assumed to be nil :—

STATEMENT No. X.

VARIETY.	Area acre.	Sucrose mean %	Difference between Duplicates.	Weighted Difference $d$ .	$d^2$ .
Chinia ...	$\frac{1}{16}$	11.55	.10	.13	.0169
Do. ...	$\frac{1}{8}$	10.40	.03	.04	.0016
Do. ...	1	11.00	.20	.27	.0729
Mungo ...	$\frac{1}{16}$	13.77	.05	.05	.0025
Do. ...	$\frac{1}{4}$	12.75	.30	.35	.1225
Khari ...	$\frac{1}{16}$	13.34	.06	.07	.0049
Do. ...	$\frac{1}{4}$	12.01	.32	.40	.1600
Do. ...	1	12.96	.23	.27	.0729
Do. ...	1	13.38	.26	.29	.0841
Bhurli ...	1	20.64	.19	.14	.0196
Ekri ...	1	13.50	.29	.32	.1024
Bansgira ...	$\frac{1}{4}$	16.61	.30	.27	.0729
					$\Sigma d^2 = .7332$

$$r = .4769 \sqrt{\frac{.7332}{12}} = \pm .118$$

which may be taken as the best value one can at present deduce for the probable error of any determination of the percentage of sucrose in the juice of a sample of cane taken in the manner described from areas up to 1 acre. The probable error  $\pm .118$  indicates that the probability of an error exceeding  $\pm .5$  is only 5 in 1,000 samples.

\* Merriman, p. 103. Collins conf., *ante*.

## THE VALUE OF SMALLER SAMPLES.

After finding at Pusa that the probable error of a sample which included about 200 canes was so small, it was decided that the best check on its reliability would be to take considerably smaller samples. The value of the probable error is expected to vary inversely as the square root of the number of canes; thus it should be doubled if the number of canes were reduced to one-fourth. Accordingly duplicate samples of about 50 canes, taken in the same manner as before, that is three canes from about 16 or 18 places uniformly distributed over the plot, were employed and the following results obtained :—

## STATEMENT NO. XI.

*Comparison of small with large samples.*

Variety.	Area acre.	Number of canes in each sample.	Juice. % <i>r</i>	Sucrose. % <i>r</i>	Glucose. % <i>r</i>
China (Pusa) ..	1 {	$\begin{matrix} 186 \\ 168 \end{matrix}$	$65.7 \pm .36$	$11.0 \pm .12$	$1.40 \pm Nil.$
Ditto ..	1 {	$\begin{matrix} 47 \\ 47 \end{matrix}$	$67.1 \pm .12$	$11.19 \pm .30$	$1.35 \pm .071$
Mungo (Pusa) ...	$\frac{1}{4}$ {	$\begin{matrix} 188 \\ 189 \end{matrix}$	$58.1 \pm .84$	$12.75 \pm .18$	$.94 \pm .018$
Ditto ...	$\frac{1}{4}$ {	$\begin{matrix} 48 \\ 47 \end{matrix}$	$59.67 \pm .02$	$13.23 \pm 1.27$	$.67 \pm .118$
Khari (Pusa) ...	1 {	$\begin{matrix} 214 \\ 215 \end{matrix}$	$64.25 \pm .90$	$12.96 \pm .14$	$1.20 \pm .143$
Ditto ...	1 {	$\begin{matrix} 48 \\ 48 \end{matrix}$	$66.00 \pm .24$	$13.66 \pm .11$	$.99 \pm .179$
Khari (Parsa)¶ ...	1 {	$\begin{matrix} 212 \\ 216 \end{matrix}$	.....	$13.38 \pm .15$	.....
Ditto ...	1 {	$\begin{matrix} 54 \\ 54 \end{matrix}$	.....	$14.61 \pm .18$	.....
Bhurli (Parsa) ...	1 {	$\begin{matrix} 210 \\ 210 \end{matrix}$	.....	$20.64 \pm .11$	.....
Ditto ...	1 {	$\begin{matrix} 45 \\ 45 \end{matrix}$	.....	$19.86 \pm .36$	.....
Ekri (Parsa) ...	1 {	$\begin{matrix} 205 \\ 204 \end{matrix}$	.....	$13.50 \pm .17$	.....
Ditto ...	1 {	$\begin{matrix} 52 \\ 54 \end{matrix}$	.....	$12.44 \pm .51$	.....
Striped Tana (Parsa) ...	$\frac{1}{4}$ {	$\begin{matrix} 186 \\ 180 \end{matrix}$	.....	$16.61 \pm .18$	.....
Ditto ...	$\frac{1}{4}$ {	$\begin{matrix} 48 \\ 48 \end{matrix}$	.....	$16.65 \pm .30$	.....

Thus so far as can be demonstrated by any small series of tests, these show almost uniformly a marked increase in the error when the size of the sample is seriously reduced below 200 canes, a result which naturally increases the dependence that may be placed on the deduction in regard to the necessary size of the sample. The probable errors in the percentage of juice form the chief exception, but a bullock-power sugarcane mill is too imperfect an implement for accurate work and its results cannot be allowed the same weight that the other determinations deserve.

The probable error of a single sample, when only about 50 canes are taken, is, after weighting the individual values for 15% sucrose,  $\pm 508$ , or an error of about  $\pm 2.0$  might be expected in 5 out of 1,000 samples.

With these some of the tests which were made in 1910 and 1912 may be compared. Here bundles of three canes each were tested separately and the mean percentage of sucrose and its probable error ascertained. The comparison is not a rigid one because the percentage of sucrose was not "weighted" for the variation in weight of cane and proportion of juice, which is in effect done when the whole lot of cane is crushed together as in the 1913 samples, but the effect of this difference in the treatment of the data could not materially affect the values of the probable error. The data are set out in the following statement No. XII from which it is seen that the error is of approximately the same magnitude as that for samples of about 50 canes tested in 1913.

#### STATEMENT No. XII.

*Showing results of tests made in 1910 and 1912 when  
units of 3 canes were taken.*

Variety.			Area acre.	Number of canes.	Sucrose. % $r_0$
Ashy Mauritius	...	...	.077	45	21.80 $\pm$ .32
Ditto	...	...	.103	60	20.99 $\pm$ .24
Purple Mauritius	...	...	.103	60	19.11 $\pm$ .19
Ditto	...	...	.103	60	18.62 $\pm$ .17

## STATEMENT No. XII.—(Continued.)

Variety.			Area acre.	Number of canes.	Sucrose, %      r.
Red Mauritius	...	...	·103	57	13·60 ± ·47
Ditto	...	...	·077	45	15·32 ± ·15
Ditto	...	...	·250	36	15·08 ± ·21
Striped Tana	...	...	·052	30	15·03 ± ·25
Ditto	...	...	·129	72	13·92 ± ·11
Hemja	...	...	·250	48	14·16 ± ·46
Ketar	...	...	·250	48	13·90 ± ·32
Mungo	...	...	·250	48	15·20 ± ·32
Khari	...	...	·250	48	15·48 ± ·32

Naturally some experimenters with sugar-cane may be able to grow cane considerably more uniform in quality than the Pusa or Parsa varieties or those which are quoted from Java. Supposing for example the individual variation in sucrose were not greater than  $\pm 1\cdot0$ , then calling the Pusa and Parsa variation

$$\left( \frac{1\cdot92 + 1\cdot92 + 1\cdot53 + 1\cdot18 + 1\cdot81 + 2\cdot19 + \cdot92}{7} \right) = 1\cdot64$$

(ex Statements V & VII)

it would be reasonable to expect that the sample might be reduced to about  $\left( \frac{1\cdot0}{1\cdot64} \right)^2 \times 200 = 74$  canes, taken as uniformly over the plot as possible.

For the sampling of very small plots, such as a few stools only of one variety, nothing definite can be said except that either a very high proportion of the whole would have to be crushed or a large series of individual canes must be tested in order to obtain a reliable mean value for the whole.

It is of interest to examine the errors which are involved when much larger quantities of cane are taken as the sample. At Partabgarh\* the method adopted by Mr. Clarke was to

\* Pusa Agricultural Research Institute Bull. No. 27.



cut out the whole of every fourth row of the plot and to crush this. Such samples weighed from about 500 to more than 1,200 lbs. of cane from 1/10 acre plots, the crushing of which was executed as rapidly as possible. The data published admit of the probable error of the individual sample being calculated, and these, in the case of the sucrose, are set out in the following statement No. XIII.

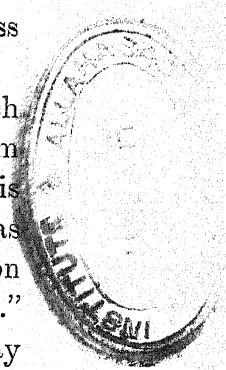
## STATEMENT No. XIII.

*Showing the probable error in the sucrose of samples of cane at Partabgarh.*

PLOT No.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	XI.
1908-1909 ... ..	$\pm 17$	$\pm 13$	$\pm 37$	...	$\pm 16$	$\pm 17$	$\pm 18$	$\pm 27$	$\pm 11$	$\pm 13$	$\pm 13$
1909-1910 ... ..	$\pm 15$	$\pm 18$	$\pm 24$	$\pm 12$	$\pm 26$	$\pm 06$	$\pm 10$	$\pm 14$	...	...	...
1910-1911 ... ..	$\pm 16$	$\pm 30$	$\pm 16$	$\pm 13$	$\pm 14$	$\pm 10$	$\pm 15$	...	...	...	...

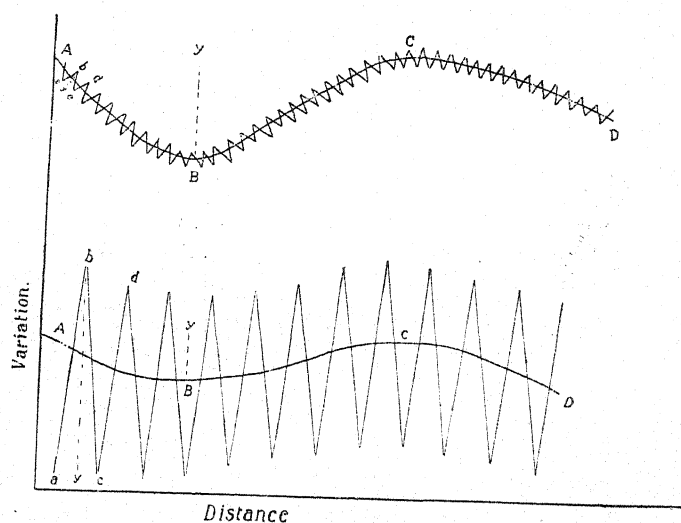
It is evident that no greater precision was attained by crushing these very much larger samples than by the use of the smaller samples at Pusa and Parsa, and one is driven to the conclusion (since it is improbable that the cane was less uniform at Partabgarh than at Pusa) that other sources of error come in when trying to deal with such large samples, which are less pronounced when dealing with small samples.

The foregoing work has not answered the question which was raised regarding the effect of "soil" as distinct from "plant" on the variability of the cane. On page 121 it is explained that the error found from duplicate samples was expected to be greater than that which represented the variation due to "plant," because it includes also the effect of "soil." In the event this has not been found to be the case. It may be that the effect of "soil" is only small. For example in the China cane, whilst the percentage of sugar varied among individual canes from 6 to 17, the maximum variation among composite samples from different parts of the field of China was



only 10.4 to 12.4, which comparison, taken rigidly, would form a proof that the effect of "soil" is only small. At the same time there is nothing to show how much or how little the "soil" affected the quality of individual canes. As has been already stated (p. 110) the idea on which the series of tests was planned was that if a series of individual contiguous canes were taken, the area of land involved would be so small, that its effect on the variation would be only nominal and might be neglected.

It may here also be emphasised that we are concerned with the effect of the soil on the variation in the plant and not directly with soil variations. The idea is set out graphically by means of the compound curve in the *upper part* of the accompanying chart. The plain curve A. D. represents such variations in the



mean quality of sugarcane as one might expect to meet with in any straight line across a field. Over this is superimposed a second curve a b c d. . . . The amplitude of this curve represents the variation due to all causes within a quite small distance such as 2 yards; it was this group of causes which was styled "plant." The amplitude of the curve A. D. represents the mean variation across the field; it would include all causes of variation, but would be obviously principally due to soil.

In the event, however, the variations have been found to be quite different from this illustration, and are more truly represented by the curves in the lower part of the chart. The variation b-y in any small distance is far greater than is the mean variation y-B across the field.

The actual area from which the 120 canes were taken was about 160 sq. ft. But the assumption that variation due to "soil" within this small area is negligibly small may be quite unsound; it may indeed for anything we know be nearly as great as in the whole field. Such a suggestion does not agree perhaps with preconceived ideas in regard to variation due to soil, but the whole of the information in regard to effect of soil on the variability of crops is in fact so limited that there is nothing unreasonable in the suggestion that it is nearly as great in 100 sq. ft. as in a whole acre. If this were so, then the variation which was ascertained from an examination of individual canes was in reality due to all causes and not to "plant" only. The assumption that the causes of variation could be isolated on which the tests were planned, would thus be shown to be impossible of achievement in practice. One other comparison may, however, still be made. If the effect of "soil" was largely included in the variation found among individual canes, then the magnitude of the error found on one acre should not be materially greater than on 1/10 acre. In point of fact it was usually somewhat greater (see Statement IX), but there are exceptions and in any case the number of instances (three) from which to judge is so small that a reliable conclusion on this point is not admissible.

In regard to the effect of "soil" on the variation of crops generally, reference may here be made to Wood and Stratton's paper, pp. 434 *et seq.*, where it is shown that for at least certain classes of experiment, the error on quite small areas such as 1/40 acre is as small as on much larger ones. The authors attribute this to the fact that whilst errors due to plant variation, weighing, measuring, etc., are reduced on a large area, the error due to soil variation is increased and that the advantages and disadvantages neutralise one another. It is, however, quite as legitimate to

argue that the variations due to "plant" and to "soil" are substantially equally great on small areas as on large ones, whilst it is certain that weighing and measuring may be made as accurately on small as on large areas. In any case the evidence that is available at present is very limited.

Will it then be suggested that, if all causes of variation are operative within an area of (say) 160 sq. ft., it is unnecessary to take cane from over the whole area in order to measure the average value of the whole crop? The answer is that it is necessary to do so. It cannot be too carefully recollected that we are dealing with variation from a mean value; not with an actual value; our object being throughout to ascertain the size of the sample which should be taken. The case is best illustrated by two examples. Consider one variety of cane growing in two neighbouring fields, the one a clayey, the other a sandy soil and of equal areas. Assume that these crops of cane are sold to one purchaser and that the price per ton is to depend on the mean quality of the cane in the two fields. Assume that the variation in each field is known to be the same, namely,  $\pm 17$ . The actual quality of the cane may, however, be quite different in the two fields; for instance, the sucrose might be, say, 2% higher in the one than in the other. The value  $\pm 17$  indicates what size of sample must be taken in order to ascertain the mean value of the cane in either field. But we desire to take *one* composite sample of the cane from the two fields, and it is obvious that one-half the sample must be taken from each field. Or again consider the case of two varieties of cane-growing in one field of the same class of soil, the areas being equal. Assume that the variation in each is known to be  $\pm 12$ . This information indicates the necessary size of the sample required in either case. If one composite sample of all the cane-growing in the field is required, it is obvious that one-half must be taken from each variety. It is in fact essential in all cases of sampling materials, whether agricultural or not, that the sample shall be made up of portions taken from every part of the whole; the size of each portion, the number of such portions, the mode in

which they are taken are, however, matters which will vary. If the mean value of a field or plot of cane is to be ascertained, portions must be taken from all over the area. This is also illustrated by the chart. It would not be correct to take the whole sample from say a few square yards about the point A, or B, although a sample of say 200 canes at either place would be sufficient to extinguish the major variation. Taken at A the sample would test too high; at B the reverse result would be experienced.

Although as has been clearly pointed out we are not dealing directly with soil variations, it is obvious that the effect of soil on variations in the plant must be closely allied to such soil variations. If these were all understood and could be stated numerically, it might be possible to compare each or some of them with the plant variations. In point of fact this is far from being possible. Reference may, however, here be made to soil nitrates. A record was maintained at Pusa some years ago of the amount of nitrate in the soil of a small field throughout a year, and one of the facts which was apparent was the very considerable variation in the amount of this constituent, at the same time, from foot to foot in the soil in any direction, laterally as well as vertically. And if the amount of nitrate varies greatly within short distances, it is reasonable to at least raise the question whether other factors of fertility do not also vary similarly.





## NOTE

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IN a former paper\* it was shown that rice varieties could be roughly distinguished by disintegrating the grains with Alkali.

In the present paper a new method is described by means of which rice varieties can be distinguished from one another by differences in the quality of their starches.

It is shown that the cooking quality of rice is correlated with starch quality.

The paper consists of two parts.

In the first part the method of fractional liquefaction for comparing rice starches as devised and tested by me is described.

The second part contains an application of the method to the differentiation of the starches of seven common rice varieties of Burma. This part of the work has been carried out in co-operation with Mr. Darabsett.

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\* Warth and Darabsett, *Pusa Agri. Res. Inst., Bull.* 38.



# THE FRACTIONAL LIQUEFACTION OF RICE STARCH

BY

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## PART I

### FRACTIONAL LIQUEFACTION OF RICE STARCHES

Starches of different cereals are generally distinguished from one another by the size, shape and optical properties of the granules.

It has been shown that they may also be distinguished by their unequal resistance towards amylolytic enzymes and in possessing different liquefaction (or so-called gelatinisation) temperatures.

Among the numerous publications showing the differential effect of enzymes upon different starches, the following by Stone<sup>1</sup>, J. O'Sullivan<sup>2</sup> and Wolff and Fernbach<sup>3</sup> are perhaps the most important.

Among the earlier determinations of the liquefaction temperatures of starches Lippmann's<sup>4</sup> figures were obtained by

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<sup>1</sup> Stone, W. E. *U. S. Agri. Dept., Office Expt. Stas. Bull.* 34, 1896.

<sup>2</sup> O'Sullivan, J. *J. C. S. Trans.*, 1904, p. 616.

<sup>3</sup> Wolff and Fernbach, *Compt. Rend.* 1907, 144, p. 645.

<sup>4</sup> Lippmann quoted by König. *Chemie der menschlichen N. & G. Mitt.*

observing with the aid of the microscope the points of incipient and complete rupture of the granules.

This method has lately been utilised for the same purpose by Nyman<sup>5</sup> who used the micropolariscope and for end point observed the disappearance of the interference crosses.

Nyman found that the younger granules were more easily ruptured than the older.

He showed also that by prolonging the action of heat the process of liquefaction took place at a lower temperature.

C. J. Lintner<sup>6</sup> studied the action of diastase on ungelatinised starch at different temperatures.

His work was continued under slightly modified conditions by Von Sigmond<sup>7</sup> who showed that considerable differences existed in the liquefaction temperatures of different starches.

More recently it has been pointed out by Wolff and Fernbach<sup>8</sup> that the starch of the pea consists of two distinct fractions.

In commencing work on the starches of rice varieties it had to be assumed that the differences to be looked for (if indeed any existed) would not be so marked as those found by experimenters who compared starches derived from very different sources.

As the methods employed by previous workers were not likely to be sufficiently precise to enable measurements to be made of relatively small differences some new method had in the first place to be devised.

I decided to compare the starches by a process of fractional liquefaction at different temperatures.

After various trials the following method was adopted.

A definite weight (usually 1 gramme) of the finely divided substance is stirred up with 70 c.c. of water and maintained at the desired temperature for one hour with regular stirring.

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5 Nyman, *Z. Unters. N. & G.* 1912.

6 Lintner, C. J.—*Woch.-Br.* 8-22 and *Chem. Centbl.*, 1890-1-500.

7 Von Sigmond. *Chem. Centbl.*, 1897-2-614.

8 Wolff and Fernbach—*Compt. Rend.*, 1905, 140.

All the starch liquefiable at that temperature is thereby converted into a paste in which the unaltered starch granules requiring a higher temperature for liquefaction remain suspended.

The liquid is cooled, water added to compensate for evaporation, 10 c.c. malt extract are run in and the conversion allowed to proceed for two hours with regular stirring at 30° C.

The unaltered starch granules presumably remain intact whilst the paste is dissolved forming maltose and dextrin. That erosion of starch granules does not take place to a measurable extent under the conditions of the experiment will be seen in the sequel.

The liquid is made up to a definite volume and filtered with kaolin.

An aliquot portion of the filtrate is hydrolysed with hydrochloric acid and the glucose content determined by Fehling solution using permanganate for estimating the cuprous oxide. From this figure the amount of starch liquefied at a given temperature may be calculated.

30° C was chosen as a convenient temperature for all conversions with malt because it is sufficiently low to give practically no erosion whilst it is high enough to allow complete conversion and to prevent the possibility of reversion.

The method resembles somewhat that employed by Lintner (*loc. cit.*), but as the object of the work differs so essentially from Lintner's enquiry one important distinction in the procedure should be remarked upon.

With the object of making the effect of the malt constant throughout, all the malt conversions in the present work were carried out at the same temperature.

Lintner malted at different temperatures because his intention was rather to study the effect of temperature upon malting.

The present enquiry was commenced before the publication of Nyman's paper, but the time factor noted upon by him was fortunately foreseen and allowed for as well as possible by maintaining a constant temperature for liquefaction for a much longer time than is usually considered necessary.

It has indeed not been proved that a still longer exposure would not yield still higher results, but one hour has given concordant duplicate figures which have a definite value, whatever future work on this time factor may reveal.

The method as described in detail above can be applied to starch samples without any difficulty, but in the present problem dealing with rice grains there is the preliminary difficulty of disintegrating the grains. This must be satisfactorily overcome before the method can be applied at all.

It has been shown by Brown and Heron that by protracted grinding starch granules become completely soluble in malt without previous liquefaction.

Therefore, to cause as little damage as possible by grinding, the grain was, in the first series of experiments, ground up with successive small quantities of water which were poured off when turbid.

The following experiment will show the extent of breakage to be expected.

Two varieties of rice were given—

- (a) the ordinary grinding with water as just described ;
- (b) a dry grinding for 45 minutes followed by wet grinding.

The samples thus obtained were liquefied at 30° and then converted at 30° with malt. The following results were obtained.

	Wet grinding.	Excessive grinding.
Sample I	6.8 c.c. (KMnO <sub>4</sub> ) Potassium Permanganate.	11.7 c.c. (KMnO <sub>4</sub> ) Potassium Permanganate.
Sample II	3.66 c.c. (KMnO <sub>4</sub> ) Potassium Permanganate.	7.7 c.c. (KMnO <sub>4</sub> ) Potassium Permanganate.

A low liquefaction temperature was chosen to bring out the effect of the grinding. It would, of course, become obscured by liquefaction at a higher temperature.

We see that the excessive grinding caused an increased liquefaction of starch, the figures being roughly twice as high as those obtained by wet grinding.



With the aid of this process of wet grinding for preparing samples, liquefaction determinations were carried out on three rice samples and one starch sample.

The grinding for each determination was done separately and as a check a duplicate determination (also with separate grinding) was made, using 20 c.c. malt.

The results of this work are shown in the accompanying table. The figures under A & B refer respectively to the results obtained with 10 and 20 c.c. malt.

*Percentage Liquefaction of Starch.*

	30°		40°		50°		60°		70°		80°	
	A	B	A	B	A	B	A	B	A	B	A	B
No. 1.	21	21	20	19	23	26	60	57	69	71	67	67
No. 2.	13	13	9	10	10	12	18	22	57	62	58	59
No. 3.	12	11	9	11	11	12	19	18	59	59	61	61
Starch	0	0	0	0	3	3	29	23	71	73	76	76

No. 1 is a glutinous rice. Nos. 2 and 3 are fairly hard non-glutinous rices.

The figures show clearly that the method when applied to starch gives concordant and interesting results.

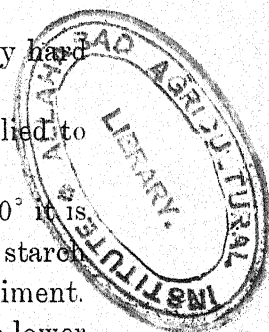
From the starch sample figures for 30°, 40°, and 50° it is evident also that no measurable erosion of unliquefied starch granules occurs under the conditions of the experiment.

We see also that the glutinous rice starch liquefies at a lower temperature than the starches of the non-glutinous rices.

The amounts of liquefaction at lower temperatures are, however, very high when compared with the starch sample which required no grinding.

It is evident, therefore, that grinding, even by the wet process, causes excessive breakage and makes the determinations at lower temperatures valueless.

Some other means of disintegration had therefore to be found.



The use of alkali for this purpose has obvious difficulties, but it was found possible eventually to disintegrate the grains satisfactorily with Potassium Hydrate in the following manner.

The weighed polished seed is placed for 24 hours in 10 c.c. of 1% Potassium Hydrate. The liquid is then made faintly acid and poured off into a beaker.

The seed is gently ground in a mortar with successive small quantities of water and the starchy liquid added to the beaker of acid liquid. Neutralisation is effected with Calcium Carbonate suspended in water.

The specimen is then ready for liquefaction and conversion as usual.

The above three rices treated in this way yielded the following results :—

		30°	40°	50°	60°
No. 1	...	7.6	6.5	8.3	65.5
No. 2	...	3.6	3.4	3.7	5.7
No. 3	...	3.0	3.2	3.5	19.8

These figures show that by means of the above alkali process the seeds can be satisfactorily disintegrated without causing appreciable breakage of the starch granules.

## PART II

## A COMPARISON OF THE STARCHES OF 7 RICE VARIETIES

The specimens examined were pure line cultures of well known types.

We disintegrated the polished seeds by the Potassium Hydrate process and carried out the fractional liquefaction determinations exactly as detailed above.

The accompanying table shows the results obtained.

TABLE I. *Fractional Liquefaction of Starch.*

Sample.	Grammes starch liquefied per 100 grm. seed at							Total* Starch.	Proteid.
	50°	55°	60°	65°	70°	75°	80°		
No. 1 ...	3.8	5.2	11.7	45.2	65.0	68.1	69.3	74.5	7.08
No. 2 ...	2.4	4.7	2.9	8.8	24.2	65.2	68.1	73.4	7.18
No. 3 ...	5.9	8.6	23.7	59.3	62.8	64.4	66.7	73.4	7.69
No. 4 ..	...	4.5	2.9	7.6	20.0	68.1	68.6	75.5	7.12
No. 6 ...	2.2	4.1	2.9	9.5	22.3	66.7	69.6	75.9	6.62
No. 8 ...	3.7	7.3	11.2	41.9	72.1	74.2	75.4	76.3	9.05
No. 9 ...	6.4	6.2	15.1	51.4	78.8†	75.6	76.3	75.9	8.39

\* Total starch in polished seed determined by official method of American Agricultural Chemists.

† This figure is evidently wrong.

The proteid content of the polished seed is shown for reference.

It should be pointed out here that the determinations of liquefied starch rest finally upon a permanganate titration.

This in itself is an exceedingly delicate and accurate determination. But to deal with large quantities for the present work is difficult and thus it comes about that in the above table 1% of starch is approximately equal to 0.1c.c. potassium permanganate. We must allow therefore that the figures in the table may be inaccurate to the extent of 1% starch.

This explains partly certain small irregularities at the lowest and highest temperatures (*i.e.*, at the points where the action had scarcely commenced and where it was practically complete).

Another possible source of error may lie in the varying strength of the malt extract employed.

The malt was not specially tested, but it was prepared each day in as uniform a manner as possible from a stock sample of green malt preserved in dessicators.

That it varied very little indeed is proved by the regularity of the results obtained and by some duplicate determinations (see below Table II). The use of standardised diastase would no doubt add to the value of such results. This will be employed in the work now contemplated.

All the determinations for one temperature were made on one day with one specimen of malt.

Concerning the amylolytic power of the seeds a remark is called for.

On the unliquefied starch (at lower temperatures) its effect is clearly negligible, and therefore it can be assumed that at the higher temperatures all the starch attacked by the combined amylolytic enzymes of the malt and the rice grains must have first of all been liquefied. That is to say, the presence of such enzymes in the rice, even if they have not been entirely destroyed by the alkali, cannot materially affect the determinations of percentage liquefaction.

It will be observed that the soluble carbohydrates (sugars, etc.) have been estimated together with and as starch.

This makes no difference to the results because if they were allowed for, it would merely mean the subtraction of a constant quantity (say 1 %) from each of the figures without altering their significance in the least.

The shape of the curves in the chart on page 144 would naturally not be affected in the smallest degree by the introduction of this correction.

There is one more point to be considered.

Some of the samples apparently contain some very resistant starch (see further on). It appeared that this resistance to liquefaction and malt conversion might possibly be due not to the nature of the starch but to incomplete action caused by imperfect disintegration of the grain. This point was tested by comparing specimens disintegrated in different ways.

The results are given in the accompanying table.

TABLE II. *Effect of disintegration on fractional liquefaction at 80°.*

Sample.	Ordinary disintegration 24 hours.	Disintegration for 48 hours.	Disintegration 48 hours with crushing after 24 hours.	Average.
No. 1	70.0	68.6	69.4	69.3
No. 2	69.4	66.7	68.1	68.1
No. 3	67.7	65.7	66.7	66.7
No. 4	70.0	67.7	68.1	68.6
No. 6	70.4	69.0	69.4	69.6
No. 8	77.1	74.2	75.0	75.4
No. 9	76.3	75.6	77.1	76.3

Clearly the ordinary disintegration process cannot be improved upon and therefore it seems fairly well established that the so-called resistant starch does actually exist. (*Cf.* Wolff and Fernbach.)

The 3 sets of determinations were made each with a separately prepared malt extract.

The table shows also therefore that the malt extracts were all very nearly equal in diastatic power.

It remains now to discuss the significance of the results obtained.

The chart on the back is a graphical representation of the series of determinations.

The three specimens 2, 4 and 6 are hard vitreous rices. The extreme similarity of their starches is remarkable.





Up to 65° they are liquefied only to a slight extent. At 70° when the other rice starches have become almost completely liquefied these three show a liquefaction of only 20%. Within the next 5 degrees, however, almost all their starch is liquefied. The sudden break-down indicates a large proportion of very uniform material.

It should be noted that in each case there is a residue of 7 or 8% of more resistant starch which only breaks down gradually.

Here the great advantage of fractional liquefaction is clearly seen.

Methods which only indicate the temperature of complete liquefaction would scarcely enable us to distinguish between samples 1 and 4 for example, whilst by fractional liquefaction a great difference is brought to light.

Of the other specimens Nos. 8 and 9 are true opaque white glutinous rices.

The starch of these specimens commences to liquefy at a much lower temperature. It is noteworthy also that these two specimens contain practically no trace of resistant starch, the liquefaction being almost complete between 70° and 75°.

No. 3 is a remarkable specimen. Its liquefaction is already far advanced at 60°. But after 65° there is very slow progress indeed and eventually it is surpassed by all the other rices.

This variety contains a fraction of very easily liquefied starch, together with 8% of more resistant starches which are liquefied in small fractions as the temperature is increased above 70°.

No. 1 is considered by the Burmans to be a semi-glutinous variety not very suitable for cooking.

Its intermediate character is revealed by its partial liquefaction at lower temperatures (similar to glutinous rice) and by the presence of a resistant fraction (similar to the hard rices).

It is grown more for sale and export than for home consumption.

That the cooking quality of rice is distinctly correlated with its starch quality is clearly proved by these results.

Attention has been called in a previous paper\* by us to the fact that rice varieties could be distinguished from one another by disintegration with alkali.

To determine how far such disintegration is correlated with the quality of the starch these rices were treated with alkali as already described.

The result is shown in the Plate.

It is evident that the disintegration does roughly correspond with the starch quality.

The three hard rices Nos. 2, 4 and 6 are not so easily attacked as the other specimens.

Again No. 3 which contains much easily liquefied starch is also most easily disintegrated.

Obviously the ease of disintegration cannot depend upon starch quality alone. Indeed the earlier stages of the process (at low concentrations of alkali) are probably quite independent of the starch quality. The parallelism found to exist between disintegration and starch quality therefore seems in some cases at least to indicate a relationship between starch quality and proteid quality. To establish such a relationship, if it exists at all, will demand observations on many more samples extending over several years.

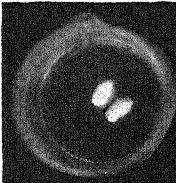

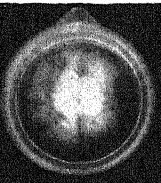
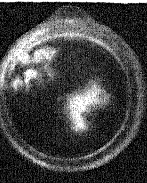
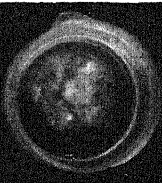
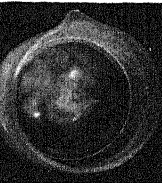
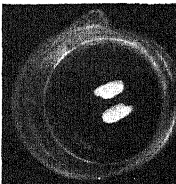



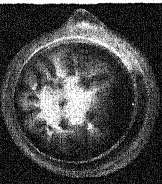
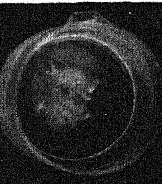
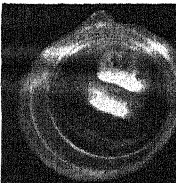
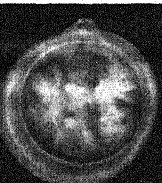
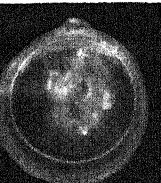
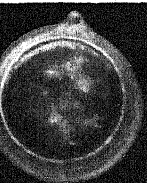
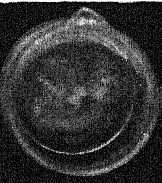
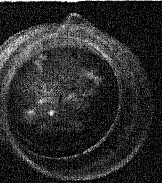
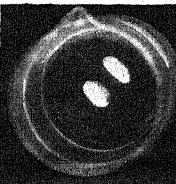



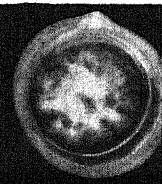
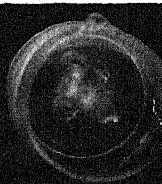
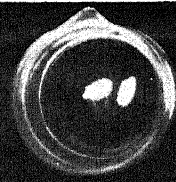
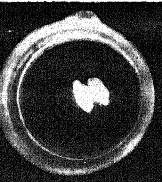
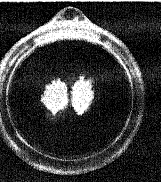

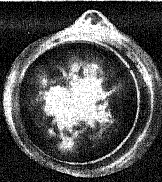

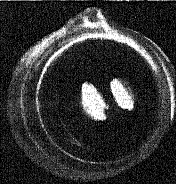
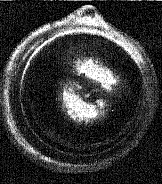


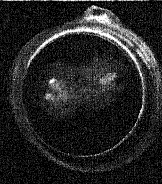
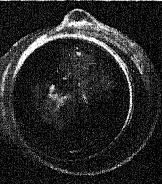

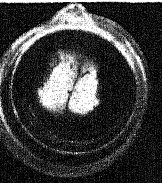
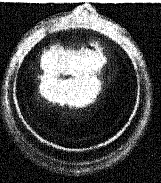

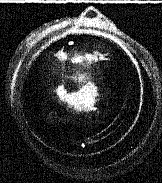

It should be noted that the parallelism referred to above is, as might have been expected, far from complete in every case. This may be seen by comparing for instance the disintegration of samples 1, 8 and 9 with the corresponding liquefaction data.

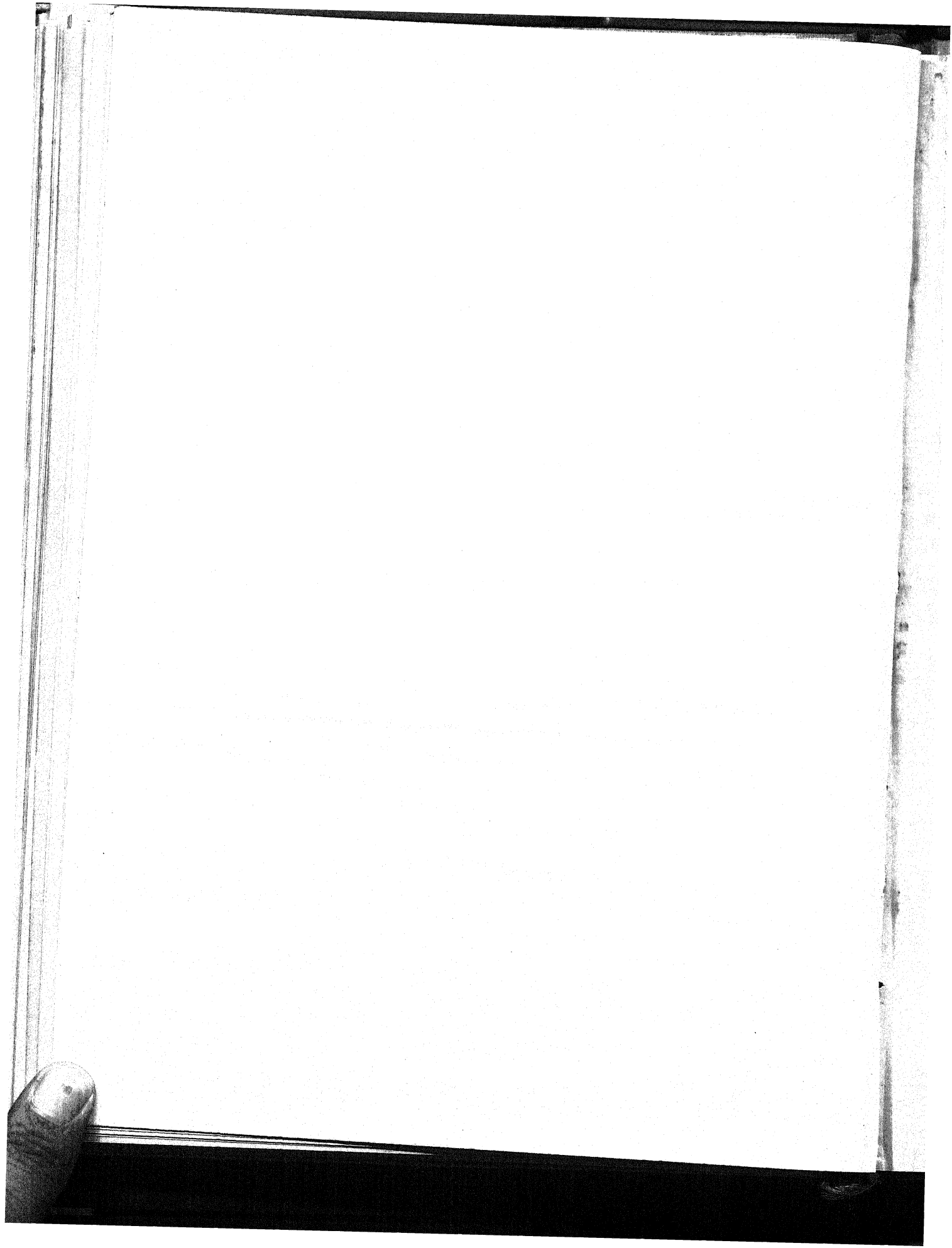
The work described in this paper is being continued to determine the effect of environment upon starch quality.

A reference to Table I shows that there is no very obvious relationship between quality of starch and quantity of proteid. Some light may possibly be shed on this point also when the effect of environment is studied.

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\* Warth and Darabsett. *Pusa Agri. Res. Inst. Bull.* 38.

	ACTION OF ALKALI ON THE SEVEN PADDY VARIETIES.					
	1% KOH	1.25% KOH	1.5% KOH	1.75% KOH	2% KOH	2.25% KOH
1						
2						
3						
4						
6						
8						
9						



## P R E F A C E

AS DR. LEATHER has kindly insisted on my name appearing on the cover of this Memoir, I feel bound to explain that my share in its production was limited to arrangements at the dairy for a portion of the tests and to arm-chair criticism from the farmer's point of view.

The whole of the work, involving a very large number of mathematical calculations, was done by Dr. Leather, and cannot have been in any way facilitated by my collaboration.

A. C. DOBBS.





# THE YIELD AND COMPOSITION OF THE MILK OF THE MONTGOMERY HERD AT PUSA, AND ERRORS IN MILK TESTS

BY

J. WALTER LEATHER, V.D., Ph.D., F.I.C.,

AND

A. C. DOBBS.

IN 1911 it was decided to make some careful tests of the yield and composition of the milk of the Montgomery or Saniwahl cattle, which is the breed maintained at Pusa. Ordinarily in India the recorded yield is that which is obtained in the usual course of milking when the calf takes at the same time an unknown quantity of milk; such records are necessarily inaccurate. Again the records of the composition of the milk that had been kept at Pusa, had been made by the dairyman and their accuracy was open to suspicion. It was decided therefore to endeavour either to avoid these and other sources of error or at least to measure their magnitude.

The tests were conducted over a period of several weeks in each case, which is longer than in most other recorded experiments.

It will be convenient firstly to consider the sources of error and subsequently to consider the data obtained.

## SOURCES OF ERROR.

(i) *Period of time between milkings.*—It is well established that the periods of time which elapse between any two milkings will affect the yield and composition of the milk. If the cow is milked twice in the 24 hours and, for example, the day period is shorter than the night period, the yield will be smaller and the

percentage of fat greater at the evening milking than if the periods were equal. This source of error must either be avoided or allowed for. For the purposes of the Pusa tests it was avoided by making the milking periods equal; the variation of time from an exact 12-hour period has not been more than 5 minutes, which is a negligible quantity.

(ii) *The calf sucks at the same time as the cow is hand-milked.*—It has been recognised that the fact of the calf sucking at the same time as the cow is hand-milked introduces an error, but so far as we are aware no attempt has been made either to negative this error or to ascertain its value. For the tests at Poona<sup>1</sup> "the calf was allowed to take as little milk as possible" which leaves the magnitude of the error as uncertain as though no attempt were made to avoid it.

Attempts have been made by European dairymen in India to train cows to allow themselves to be hand-milked in the absence of the calf. Colonel Hallowes, Director of Military Farms and Mr. Smith, Assistant Director of Dairy Farms, inform us that in some of the Military Dairies considerable success in this matter has been achieved with half-bred Ayrshire-Indian and with Sind cattle, but that with other breeds the difficulty has not been overcome. Buffaloes frequently present less difficulty. Attempts to overcome the difficulty with the Montgomery cows at Pusa failed. Under the circumstances it seemed to us better to try to obtain accurate data with as little disturbance of this Indian custom as possible. If for example the one side of the udder were hand-milked whilst the calf sucked the other as is the practice at Pusa, it was reasonable to hope that either exactly one-half of the milk would be obtained by hand, and that half of average quality, or that at least such a method would admit of the error being estimated. In point of fact this method has proved quite successful; as will be seen, one-half of the milk is actually obtained under such conditions, and the error due to the calf sucking has been negated

<sup>1</sup> See Meggitt & Mann, *Memoirs Dept. of Agri., India*, Chem. Ser. Vol. II, No. 1.

during the trials, excepting one month (October) when an attempt was made to estimate its magnitude.

(iii) *Analytical errors.*—The magnitude of these is well-known to be much smaller than that due to other causes. The fat percentage was determined by Gerber's method. A series of 16 samples was tested also by extraction with ether, using the Adams' coil, as a check on the Gerber bottles, which showed that the latter frequently gave  $\cdot 1\%$  fat too low, this error being largely systematic. No correction has been made for it, since it is insignificant in comparison with other sources of error.

#### GENERAL PLAN OF THE TESTS.

The tests were conducted during three periods : (A) December 3rd, 1911, to January 31st, 1912 ; (B) March 28th to June 1st, 1912 ; (C) September 1st to November 9th, 1912.

The following list of the cows indicates the age of the calf in each case :—

Period.	Cow.	Date of calving.	Relative yield.
A	No. 51 Khaki	30th Sept. 1911	Reduced to $\frac{3}{4}$ yield.
	No. 88 Subhagi	24th Augt. 1911	Do.
	No. 91 Amiri	30th Octr. 1911	In full milk.
B	No. 159 Kamali	17th Mar. 1912	In full milk.
	No. 128 Nami	30th Jany. 1912	Do.
	No. 101 Radhi	16th Jany. 1912	Reduced to $\frac{3}{4}$ yield.
	No. 99 Godhi	15th Decr. 1911	Reduced to $\frac{3}{4}$ yield.
	No. 44 Moghi	11th Jany. 1912	In full milk.
	No. 67 Nathali	25th Decr. 1911	Reduced to $\frac{3}{4}$ yield.
	No. 78 Rami	6th Feby. 1912	In full milk.
	No. 95 Janki	12th Jany. 1912	Do.
	No. 133 Kaveri	15th Jany. 1912	Reduced to $\frac{1}{2}$ yield.
	No. 85 Gilori	27th Decr. 1911	Reduced to $\frac{1}{2}$ yield.
	No. 33 Boudhi	1st Mar. 1912	Do.
	No. 30 Gujri	29th Jany. 1912	Do.
C	No. 160 Thoosri	21st Mar. 1912	Going off.
	No. 130 Tikya	5th July 1912	In full milk.
	No. 161 Mayani	13th Augt. 1912	Do.
	No. 31 Balli	25th June 1912	Reduced to $\frac{3}{4}$ yield.
	No. 97 Kesari	5th June 1912	In full milk.
	No. 36 Gongli	29th June 1912	Do.
	No. 42 Chikni	27th July 1912	Reduced to $\frac{3}{4}$ yield.
	No. 56 Padmini	2nd July 1912	In full milk.
	No. 50 Bhadki	18th June 1912	Reduced to $\frac{3}{4}$ yield.
	No. 15 Hoosni	15th June 1912	In full milk.

*Hours of milking.*—All the cows which were under observation at any time were milked about 5 A.M. and 5 P.M., the time interval being 12 hours with a variation of not more than 5 minutes.

*Period A.*—The cows were milked thus:—From December 5th to 22nd one-half of the udder was milked by hand, the other half being sucked by the calf. Commencing, say, with the right side (hand-milked) on December 4th morning and evening, this was followed on December 5th by hand-milking the left side morning and evening. On December 6th the right side was hand-milked morning and evening, and this sequence was followed until December 22nd. Thus during this half period the first milking by hand on either side of the udder was in the morning. Then during the 2nd half period from January 3rd to 31st the system of milking was the same, *excepting* that the first milking by hand from either side was in the evening; thus, say, on January 3rd evening, the left side was hand-milked followed again on January 4th morning by hand-milking the left side; January 4th evening the right side was hand-milked and again this same side was hand-milked on January 5th morning. Thus during the second half period the first milking by hand on either side of the udder was in the evening. The reason for making the change of side at the morning milking in December and at the evening milking in January was to distinguish between possible errors due on the one hand to the calf leaving milk in its half udder, or to the milkman imperfectly milking his side, and on the other hand to a difference in the rate of milk secretion by day and night respectively. This matter is referred to again subsequently.

Further, during this period the milk of the fore-quarter of the udder was drawn (by hand) separately from that of the rear quarter. By this system of separation some very interesting data were obtained. There was moreover with the three cows which were being tested no sign that this mode of milking caused any unknown errors. Nevertheless, partly because of the risk that such might occur, and partly because a knowledge of the quantity and quality

of the milk from the several quarters of the udder was distinct from the principal objects which we had in view, this mode of milking was not repeated in the subsequent periods B and C.

*Period B.*—Twelve other cows were tested. The system of milking was the same as during Period A, *excepting* that the milk of the two quarters of the udder on the one side or the other was hand-drawn together, which made the system of milking more normal. During April the first hand-milking from either side was in the morning, the second in the evening; during May the first hand-milking was in the evening and the second in the morning from that side.

*Period C.*—The object of Period C was to ascertain what errors were involved by hand-milking in the ordinary way when the cows are milked for profit and when as much is obtained as possible without starving the calf. Ten cows, all again different from those of Periods A and B, were brought under observation. The period was divided into three parts: C<sub>1</sub> September 1st to 28th, C<sub>2</sub> September 29th to October 26th, C<sub>3</sub> October 28th to November 9th.

During sub-period C<sub>1</sub>, the cows were milked as during Periods A and B, *i.e.*, they were hand-milked from one side of the udder, the calf taking the milk of the other half; the change of side was made in the morning. During sub-period C<sub>2</sub> the cows were milked as for profit, no differentiation being made as to the side of the udder in respect either of hand-milking or of what the calf sucked. During sub-period C<sub>3</sub> the cows were milked as during sub-period C<sub>1</sub>.

#### DATA OBTAINED.

In considering the data which have been obtained, it will be most convenient if they are sub-divided as follows:—

##### *Yield of milk.*—

Mean yield of milk morning and evening respectively.

Mean yield of milk from each half udder.

Error of the mean.

Error of the individual milking.

The total production of milk of each cow.

##### *Composition of milk.*—

Mean % fat in milk.

Error of the mean.

Error of the individual milking.

Difference of % fat from different sides of the udder.

Difference of % fat from different quarters of the udder.

Difference of % fat in morning and evening milk.

Errors involved when milking in the ordinary way.

Effect of meteorological conditions.

“Complete” analyses of milk of Montgomery cows.

#### YIELD OF MILK.

*Sources of error.*—The first question was whether hand-milking and the sucking of the calf were equally efficient in draining the udder. If not, the amount obtained by hand-milking and weighed, would vary systematically according as a hand-milking followed the calf or a previous hand-milking. Such a variation might be obscured by any variation in the amount of milk secreted by day and by night respectively. But by shifting the change from sucking to hand-milking from night time to day time as was done,



any systematic difference due to these two causes that were additive in the first half period would tend to cancel one another in the second and *vice versa*, and we should get at least during one half period a considerable difference between the amount of the morning and evening milk. But there were no such considerable systematic differences, and in fact the amounts of milk obtained from the same side of the udder in the morning and evening during each period were remarkably similar—showing that neither the method of drawing the milk nor the period—whether of day or night—after which it was drawn, affected the amount significantly in the case of any of the cows tested.

If to these conclusions is added the fact that most of the differences between successive milkings were quite small, it becomes evident that the conclusion, that the mean yields shown in Statement II are not materially affected by these sources of error, is perfectly justified. It is the first occasion that an attempt has been made to exclude or estimate the effect of the calf-sucking at the same time as a cow is hand-milked during dairy trials in India. The result is that (i) under the conditions we have employed, just one-half the milk was obtained by hand whilst the calf took the other half, and (ii) it becomes possible to detect from our records any systematic differences in the yield of milk from the several parts of the udder.

*Quantity of milk morning and evening.*—In Statement I are set out the average yields of milk obtained morning and evening from each cow. Each datum is the mean of two half periods and any error due to the fact of the morning or evening milking succeeding a hand-milking or calf-sucking is more perfectly obliterated than would be the case if the averages for each month were separately set out. Thus the morning average for cow Khaki 3.50 lbs. is the mean of 3.69 lbs. in December and 3.30 lbs. in January. During December the morning hand-milking followed the calf sucking, whilst during January it followed the hand-milking of the previous evening.

*Statement I.—Showing AVERAGE YIELDS (lbs.) of milk MORNING and EVENING obtained from half udder by hand.*

Period.	Cow.	Month.	Morning.	Evening.
A	Khaki ..	December & January	3.50	3.63
	Subhagi ..	Do.	3.02	3.03
	Amiri ..	Do.	3.35	3.21
B	Kamali ..	April & May	2.66	2.61
	Nami ..	Do.	2.40	2.58
	Radhi ..	Do.	2.55	2.53
	Godhi ..	Do.	2.90	3.02
	Moghi ..	Do.	2.67	2.68
	Nathali ..	Do.	2.96	3.04
	Rami ..	Do.	3.21	3.27
	Janki ..	Do.	2.50	2.67
	Kaveri ..	Do.	2.83	2.98
	Gilori ..	Do.	2.57	2.68
	Boudhi ..	Do.	3.23	3.32
	Gujri ..	Do.	2.60	2.63
C <sub>1</sub> C <sub>2</sub> .	Thoosri ..	September & November	1.62	1.57
	Tikya ..	Do.	2.01	1.98
	Mayani ..	Do.	2.69	2.63
	Balli ..	Do.	2.74	2.76
	Kesari ..	Do.	2.84	2.85
	Gongli ..	Do.	3.02	3.05
	Chikni ..	Do.	3.39	3.35
	Padmini ..	Do.	3.84	3.81
	Bhadki ..	Do.	4.66	4.64
	Hoosni ..	Do.	5.29	5.44

An examination of these data shows that there was no systematic difference; in fact, the yields have been in this respect very equal.

In this connection Crowther\* quotes records obtained at Garforth in Yorkshire and at Offerton in Northumberland in which cows yielded very much more milk during the night time. These tests were not made at 12-hour intervals as were the Pusa tests, but even allowing for difference of system in milking, there seems little doubt that whilst some herds under one set of conditions may yield equal quantities of milk during the day and night respectively, other herds may not do so.

*Quantity of milk from the two sides of the udder.*—In Statement II a comparison is drawn between the yields of milk from the two

\* C. Crowther, *Jour. Agr. Sci.*, I, 154.

*Statement II.—Showing AVERAGE YIELDS (lbs.) per 24 hours † of milk from the LEFT and RIGHT SIDE of the udder of each cow.*

	Cow.	Month.	Period. days.	Left side.		Right side.		Total. lbs.	Weighted mean production. lbs.
				lbs.	r.	lbs.	r.		
Period A.	No. 51 Khaki	Deer. Jany.	17 29	*7.90 ± .150 *7.17 ± .063		7.15 ± .280 6.29 ± .073		15.05 13.46	14.05
	No. 88 Subhagi	Deer. Jany.	17 29	6.01 ± .091 5.08 ± .063		*7.11 ± .042 *6.07 ± .064		13.12 11.15	
	No. 91 Amiri	Deer. Jany.	17 29	7.14 ± .195 6.07 ± .100		7.09 ± .181 6.02 ± .060		14.23 12.09	
Period B.	No. 159 Kamali	Apr. May	30 31	4.53 ± .048 5.05 ± .057		*5.45 ± .115 *6.07 ± .076		9.98 11.12	10.55
	No. 128 Nami	April May	30 31	4.98 ± .063 5.17 ± .063		4.83 ± .085 4.95 ± .065		9.81 10.12	
	No. 101 Radhi	April May	30 31	4.87 ± .084 5.50 ± .098		4.60 ± .056 5.35 ± .128		9.47 10.85	10.16
	No. 99 Godhi	April May	30 31	5.90 ± .089 6.12 ± .069		5.66 ± .099 6.02 ± .094		11.56 12.14	
	No. 44 Moghi	April May	30 31	4.07 ± .076 4.62 ± .133		*6.45 ± .066 *6.30 ± .051		10.52 10.92	10.72
	No. 67 Nathali	April May	30 31	5.90 ± .054 6.18 ± .066		5.93 ± .071 6.02 ± .051		11.83 12.20	
	No. 78 Rami	April May	30 31	6.42 ± .080 6.60 ± .072		6.25 ± .075 6.70 ± .059		12.67 13.30	12.98
	No. 95 Janki	April May	30 31	4.73 ± .065 5.20 ± .084		*5.27 ± .057 5.50 ± .038		9.80 10.70	
	No. 133 Kaveri	April May	30 31	5.93 ± .061 5.73 ± .065		5.92 ± .103 5.65 ± .084		11.85 11.38	11.62
	No. 85 Giloni	April May	30 31	4.85 ± .077 5.43 ± .063		*5.20 ± .063 5.52 ± .059		10.05 10.95	
	No. 33 Boudhi	April May	30 31	6.22 ± .068 6.10 ± .089		*7.25 ± .060 *6.62 ± .047		13.47 12.72	13.09
	No. 30 Gujri	April May	30 31	4.85 ± .074		*5.82 ± .048		10.67	
Period C.	No. 160 Thosri	Sept. Oct.-Nov.	28 14	3.60 ± .06 *2.68 ± .09		3.64 ± .06 2.11 ± .14		7.24 4.79	6.42
	No. 130 Tikya	Sept. Oct.-Nov.	28 14	4.06 ± .04 *4.11 ± .08		4.00 ± .02 3.71 ± .07		8.06 7.82	

† This 24-hour period refers to the 1st and 2nd milking from the one side of the udder; it is not a calendar day.



*Statement II.—continued.*

	Cow.	Month.	Period days.	Left side		Right side		Total. lbs.	Weighted mean production. lbs.
				lbs.	r.	lbs.	r.		
Period C.	No. 161 Mayani	Sept. Oct.-Nov.	28 14	5.42 ± .06 4.89 ± .19		5.52 ± .08 5.15 ± .11		10.94 10.04	10.65
	No. 31 Balli	Sept. Oct.-Nov.	28 14	6.08 ± .04 4.32 ± .07		6.09 ± .04 4.46 ± .14		12.17 8.78	
	No. 97 Kesari	Sept. Oct.-Nov.	28 14	6.21 ± .05 4.75 ± .07		6.09 ± .07 4.75 ± .06		12.30 9.50	11.37
	No. 36 Gongli	Sept. Oct.-Nov.	28 14	6.23 ± .04 5.89 ± .05		6.20 ± .04 5.86 ± .05		12.43 11.75	
	No. 42 Chikni	Sept. Oct.-Nov.	28 14	7.67 ± .07 4.82 ± .11		7.61 ± .06 *5.25 ± .15		15.28 10.07	13.54
	No. 56 Padmini	Sept. Oct.-Nov.	28 14	8.27 ± .07 6.11 ± .07		8.36 ± .08 6.43 ± .08		16.63 12.54	
	No. 50 Bhadki	Sept. Oct.-Nov.	28 14	9.90 ± .08 8.32 ± .07		9.84 ± .08 8.11 ± .12		19.74 16.43	18.64
	No. 15 Hoosni	Sept. Oct.-Nov.	28 14	11.73 ± .16 8.82 ± .12		11.80 ± .15 8.71 ± .25		23.53 17.53	

halves of the udder, namely, the left and right sides. A careful scrutiny of the data shows that in certain cases the yield was greater by more than .3 lb. on the one side than on the other; such instances are marked \*; smaller differences are considered accidental.

Thus cow Khaki yielded .75 lb. in December and .88 lb. milk in January more from the left half udder than from the right. Cow Subhagi yielded 1.1 lb. in December and .99 lb. in January more from the right than from the left half udder. Altogether there are five such cases among the 25 cows. In addition, there are six other instances in which a cow yielded more milk from one side than from the other during one month, whilst no significant difference occurred in the other month. These latter are not systematic and must be considered accidental. Moreover, five of them are small differences; in any case their cause is not known. Of the five which are apparently systematic, four are instances of a higher

yield from the right half udder. It is of course possible that such differences are characteristic of certain cows, but they are more probably due to the local loss of function that is so common in the cow's udder and is caused by mechanical injury or sporadic inflammation. It is however clear that such differences do not occur among the majority of cows, at least in this herd. The quantities are usually equal from each side of the udder.

*The error of the mean.*—The probable error of the mean yield is shown under  $r_0$ , in Statement II, and is in most cases less than  $\pm 1$ . The arithmetical mean of these values is  $\pm 0.8$ . The conclusion may therefore be drawn that there is a probability of about 100 : 1 that these means are within .3 lb. of the truth.

*The error of the individual milking.*—The error which occurs among individual milkings is considerable. During Period A the probable error was  $\pm .29$ , for Period B,  $\pm .28$ , for Period C,  $\pm .26$ . It serves to show how necessary it is in milking trials to conduct the test over a fairly long period if reasonable accuracy is to be attained. If dependence were placed on an individual milking, the yield might readily be 1 lb. or more wrong.

*The daily production of each cow.*—The total amount of milk of each cow per day is set out in the last column of Statement II and is obtained from the sum of the yield of the left and right half udders. It has been already explained why this summation is dependable, and it is only here necessary to remind the reader that this is the total production, and not the amount actually obtainable under Indian conditions. The latter is discussed subsequently. A consideration of these quantities shows that during Periods A and B the differences between the daily production for the two half-periods respectively, that is the differences between the quantities for December and for January, and between those for April and May respectively in any one case, varied from about .5 lb. up to 2.0 lbs.; those for Period C are greater in some cases, the variation then being from less than .5 lb. up to as much as 5 lbs. These will be referred to later. The last column of Statement II

contains the mean production for each cow, from which it is seen that the quantity for the period of these tests varied from 6.4 lbs. to 21.5 lbs.

### COMPOSITION OF THE MILK.

The % fat was determined in samples of the milk daily; in addition more complete analyses were made in some samples which are referred to subsequently.

*Statement III.—Showing mean percentage of FAT in cows' milk for the LEFT and RIGHT HALVES of udder, MORNING and EVENING respectively, and the value of the probable error  $r_o$ , of each.*

Cow.	Month.	Period days.	LEFT SIDE.		RIGHT SIDE.		Weighted mean % Fat.
			Morning.	Evening.	Morning.	Evening.	
			Fat% $r_o$	Fat% $r_o$	Fat% $r_o$	Fat% $r_o$	
Khaki {	Decr. Jany.	17	4.85 $\pm$ .11	3.98 $\pm$ .07	4.85 $\pm$ .14	3.98 $\pm$ .09	4.33
		29	4.63 $\pm$ .07	4.12 $\pm$ .05	4.62 $\pm$ .03	3.74 $\pm$ .05	
Sub-hagi {	Decr. Jany.	17	4.82 $\pm$ .07	3.75 $\pm$ .05	4.90 $\pm$ .17	4.30 $\pm$ .20	4.46
		29	4.96 $\pm$ .08	4.00 $\pm$ .08	4.79 $\pm$ .10	4.10 $\pm$ .08	
Amiri {	Decr. Jany.	17	4.56 $\pm$ .04	3.84 $\pm$ .07	4.55 $\pm$ .01	3.95 $\pm$ .11	4.24
		29	4.77 $\pm$ .03	3.95 $\pm$ .05	4.46 $\pm$ .06	3.80 $\pm$ .04	
Kamali {	April May	30	4.69 $\pm$ .10	3.50 $\pm$ .09	4.91 $\pm$ .07	3.43 $\pm$ .08	4.21
		31	4.73 $\pm$ .06	3.52 $\pm$ .07	5.30 $\pm$ .06	3.62 $\pm$ .07	
Nami {	April May	30	5.13 $\pm$ .09	4.28 $\pm$ .06	5.18 $\pm$ .12	4.35 $\pm$ .06	4.88
		31	5.53 $\pm$ .05	4.63 $\pm$ .06	5.44 $\pm$ .07	4.57 $\pm$ .03	
Radhi {	April May	30	4.64 $\pm$ .11	3.46 $\pm$ .06	4.90 $\pm$ .12	3.83 $\pm$ .07	4.13
		31	4.82 $\pm$ .07	3.96 $\pm$ .06	5.02 $\pm$ .16	4.04 $\pm$ .07	
Godhi {	April May	30	4.20 $\pm$ .05	3.00 $\pm$ .03	4.01 $\pm$ .09	2.87 $\pm$ .05	3.53
		31	4.11 $\pm$ .06	3.04 $\pm$ .04	4.22 $\pm$ .08	2.90 $\pm$ .04	
Moghi {	April May	30	4.75 $\pm$ .13	3.66 $\pm$ .12	5.48 $\pm$ .26	3.73 $\pm$ .10	4.43
		31	4.94 $\pm$ .12	3.72 $\pm$ .09	5.36 $\pm$ .16	3.83 $\pm$ .11	
Nathali {	April May	30	5.33 $\pm$ .14	4.93 $\pm$ .15	5.61 $\pm$ .23	4.73 $\pm$ .10	5.23
		31	5.64 $\pm$ .12	4.94 $\pm$ .12	5.80 $\pm$ .15	4.93 $\pm$ .17	
Rami {	April May	30	4.08 $\pm$ .05	3.75 $\pm$ .08	3.98 $\pm$ .09	3.69 $\pm$ .05	4.12
		31	4.80 $\pm$ .08	4.18 $\pm$ .06	4.73 $\pm$ .10	3.81 $\pm$ .09	
Janki {	April May	30	5.25 $\pm$ .15	3.54 $\pm$ .06	5.40 $\pm$ .17	3.67 $\pm$ .04	4.48
		31	5.01 $\pm$ .09	3.78 $\pm$ .05	5.38 $\pm$ .11	3.85 $\pm$ .07	



## Statement III.—continued.

Cow.	Month.	Period days.	LEFT SIDE.		RIGHT SIDE.		Weighted mean % Fat.
			Morning.	Evening.	Morning.	Evening.	
			Fat% <i>r.</i>	Fat% <i>r.</i>	Fat% <i>r.</i>	Fat% <i>r.</i>	
Kaveri {	April	30	3.96 ± .09	2.93 ± .03	3.74 ± .09	2.97 ± .06	3.42
		31	3.91 ± .04	2.92 ± .04	4.06 ± .05	2.89 ± .02	
Gilori {	April	30	4.18 ± .09	2.75 ± .06	4.10 ± .10	2.85 ± .04	3.54
		31	4.33 ± .06	2.96 ± .04	4.31 ± .06	2.90 ± .04	
Boudhi {	April	30	4.10 ± .12	3.21 ± .06	4.36 ± .10	3.58 ± .09	3.87
		31	4.46 ± .06	3.16 ± .06	4.60 ± .10	3.50 ± .07	
Gujri {	April	30					4.76
		31	5.20 ± .16	3.89 ± .06	5.68 ± .14	4.28 ± .06	
No. 160 Thoosri {	Sept.	28	5.37 ± .17	4.40 ± .15	5.23 ± .09	4.10 ± .09	4.83
		14	5.42 ± .11	4.55 ± .19	5.15 ± .17	4.68 ± .16	
No. 130 Tikya {	Sept.	28	4.85 ± .09	4.10 ± .06	4.91 ± .09	4.15 ± .07	4.72
		14	5.38 ± .10	4.72 ± .15	5.43 ± .13	5.12 ± .09	
No. 161 Mayani {	Sept.	28	3.88 ± .06	3.26 ± .08	3.98 ± .07	3.33 ± .06	4.17
		14	5.12 ± .18	5.07 ± .21	5.88 ± .21	5.10 ± .12	
No. 31 Balli {	Sept.	28	4.90 ± .11	3.66 ± .06	4.77 ± .11	3.82 ± .06	4.48
		14	5.60 ± .14	4.07 ± .16	5.51 ± .13	4.37 ± .13	
No. 97 Kesari {	Sept.	28	3.90 ± .15	3.21 ± .10	4.04 ± .15	3.32 ± .07	4.03
		14	4.83 ± .17	4.95 ± .16	5.12 ± .20	4.62 ± .07	
No. 36 Gongli {	Sept.	28	4.20 ± .10	3.36 ± .10	4.19 ± .10	3.44 ± .10	4.05
		14	4.52 ± .10	4.40 ± .10	4.90 ± .16	4.43 ± .05	
No. 42 Chikni {	Sept.	28	4.16 ± .08	3.30 ± .05	4.59 ± .13	3.45 ± .10	4.00
		14	4.87 ± .20	3.57 ± .10	4.70 ± .17	3.88 ± .10	
No. 56 Pad- mini {	Sept.	28	4.88 ± .08	4.12 ± .05	4.84 ± .07	4.06 ± .07	4.89
		14	6.03 ± .15	5.37 ± .17	5.82 ± .17	5.53 ± .19	
No. 50 Bhadki {	Sept.	28	3.41 ± .06	3.05 ± .04	3.48 ± .08	2.90 ± .06	3.45
		14	4.03 ± .17	3.93 ± .26	4.23 ± .18	3.65 ± .14	
No. 15 Hoosni {	Sept.	28	3.58 ± .06	3.09 ± .11	3.70 ± .10	3.20 ± .10	3.51
		14	3.72 ± .10	3.68 ± .12	4.15 ± .23	3.53 ± .16	

*Mean % fat.*—The per cent. fat was determined by the Gerber method, which, as has already been mentioned, was apparently

subject to a systematic error of about  $\cdot 1\%$ . No correction was made for this because the other errors are probably greater. In Statement III are set out the mean % fat for each cow, during each sub-period, for the milk of the left and right hand sides of the udder and for morning and evening respectively, from which it is seen that the milk of this herd contains generally from 4 to 6 % of fat. This statement likewise sets out the value of the *probable error of the mean*,  $r_o$ . The errors of the mean percentage as shown in Statement III are commonly about  $\pm \cdot 1$  which gives a high probability that the mean per cent. fat is not wrong by  $\cdot 3$ . Differences greater than this amount may therefore be considered significant.

*The error of the individual milking.*—The values of the probable error for individual milkings were found to be  $\pm \cdot 22$  for Period A,  $\pm \cdot 31$  for Period B, and  $\pm \cdot 33$  for Period C. This means that there is a probability of about 1 in 24 that the % fat of any individual milking will be  $\pm \cdot 9$  in error. There is perhaps nothing very novel in this fact, for it is generally recognised that isolated tests of individual cow's milk are "doubtfully correct," but it is difficult to find data on the subject in the literature.

*The mean percentage of fat in the milk for all the cows*, after weighting for differences of period, is 4.23 which is the best value that is obtainable for the herd at Pusa.

*Difference in % fat from different sides of the udder.*—From the data contained in Statement III the percentage of fat in the milk from the left and right sides of the udder respectively may be compared. This comparison is simplified by taking the means of morning and evening in each case, as exhibited in Statement IV. Thus 4.41% (Statement IV) is the mean of 4.85 and 3.98, cow Khaki, December, left side (Statement III). In the last column of Statement IV are set out the differences between the % fat of left and right sides respectively, and these differences place it beyond doubt that they must be considered purely accidental. There are

*Statement IV.—Showing mean percentage of FAT in milk from LEFT and RIGHT SIDE of udder respectively.*

Cow.	Month.	Left side Fat %	Right side Fat %	Left side +, or — right side.
Khaki ..	December ..	4.41	4.41	± 0
	January ..	4.37	4.18	+ .19
Subhagi ..	December ..	4.27	4.60	— .33
	January ..	4.48	4.44	+ .04
Amiri ..	December ..	4.20	4.25	— .05
	January ..	4.36	4.13	+ .23
Kamali ..	April ..	4.09	4.17	— .08
	May ..	4.12	4.46	— .34
Nami ..	April ..	4.70	4.76	— .06
	May ..	5.08	5.00	+ .08
Radhi ..	April ..	4.05	4.36	— .31
	May ..	4.38	4.53	— .15
Godhi ..	April ..	3.60	3.44	+ .16
	May ..	3.57	3.56	+ .01
Moghi ..	April ..	4.20	4.60	— .40
	May ..	4.33	4.60	— .27
Nathali ..	April ..	5.13	5.17	— .04
	May ..	5.29	5.36	— .07
Rami ..	April ..	3.91	3.83	+ .08
	May ..	4.49	4.27	+ .22
Janki ..	April ..	4.38	4.53	— .15
	May ..	4.39	4.61	— .22
Kaveri ..	April ..	3.44	3.35	+ .09
	May ..	3.41	3.47	— .06
Gilori ..	April ..	3.46	3.47	— .01
	May ..	3.64	3.60	+ .04
Boudhi ..	April ..	3.65	3.97	— .32
	May ..	3.81	4.05	— .24
Gujri ..	April ..	4.54	4.98	— .44
	May ..	4.54	4.98	— .44
No. 160 Thoosri	September ..	4.88	4.66	+ .28
	November ..	4.98	4.91	+ .07
No. 130 Tikya	September ..	4.47	4.53	— .03
	November ..	5.05	5.29	— .24
No. 161 Mayani	September ..	3.57	3.65	— .08
	November ..	5.09	5.49	— .40

*Statement IV.—continued.*

Cow.	Month.	Left side Fat %	Right side Fat %	Left side + or —right side.
No. 31 Balli .. {	September ..	4.28	4.24	+ .04
	November ..	4.83	4.94	— .11
No. 97 Kesari .. {	September ..	3.55	3.68	— .13
	November ..	4.89	4.87	+ .02
No. 36 Gongli .. {	September ..	3.78	3.81	— .03
	November ..	4.46	4.66	— .20
No. 42 Chikni .. {	September ..	3.73	4.02	— .29
	November ..	4.22	4.29	— .07
No. 56 Padmini .. {	September ..	4.50	4.45	+ .05
	November ..	5.70	5.67	+ .03
No. 50 Bhadki .. {	September ..	3.23	3.19	+ .04
	November ..	3.98	3.94	+ .04
No. 15 Hoosni .. {	September ..	3.33	3.45	— .12
	November ..	3.70	3.84	— .14

altogether seven instances in which the difference exceeds .3, but in only one case, namely, cow "Moghi" could it be considered systematic. Taken as a whole the evidence is quite definite that there is no sign of any systematic difference in the quality of the milk of the two sides of the udder. Given a test over a sufficiently long period it would be safe (for cows of this herd) to depend on the milk of either side of the udder for a fair sample, though no doubt it is better to test the milk of both sides together.

*Difference in % fat in milk from different quarters of the udder.—*As has been already mentioned, the milk was drawn during December and January separately from the fore and hind-quarters. Only three cows were thus tested and consequently it is hardly safe to draw conclusions very definitely from the results.

A consideration of the *differences* shown in the upper statement or of the *numbers* in the lower statement indicates that there seem to be *characteristic* differences among cows in respect of the quality

*Statement V.—Comparison of FAT percentage in FORE and HIND-QUARTERS.*

Cow.	Month.	Mean % Fat.		Difference.	Mean % Fat.		Difference.
		L.F.	L.H.		R.F.	R.H.	
Khaki ..	December ..	4.40	4.48	H .08	4.43	4.39	F .04
	January ..	4.33	4.36	H .03	4.23	4.01	F .22
Subhagi ..	December ..	4.30	4.35	H .05	4.69	4.51	F .18
	January ..	4.54	4.27	F .27	4.68	4.25	F .43
Amiri ..	December ..	4.16	4.30	H .14	4.20	4.33	H .13
	January ..	4.23	4.33	H .10	4.04	4.22	H .08

*The number of instances when one quarter produced richer milk than another quarter.*

Cow.		Khaki.		Subhagi.		Amiri.	
December ..	..	L	R	L	R	L	R
No. of tests ..	..	13	12	13	12	13	12
F ..	..	3	1	2	6	0	1
H ..	..	4	0	4	0	7	7
January ..	..						
No. of tests ..	..	22	18	22	17	22	17
F ..	..	6	10	17	15	2	1
H ..	..	7	2	0	0	8	7

of the milk which they produce in the several quarters of the udder. Of the three cows, cow "Khaki" showed no general difference between the milk of the several quarters; cow "Subhagi" yielded milk which was very generally richer from the fore than from the hind-quarter; whilst thirdly, cow "Amiri's" milk was regularly richer from the hind-quarter than from the fore-quarter. Individual differences would not be significant unless greater than .1, because the experimental error in reading the fat percentage on the Gerber bottle is at least .05 in each of two cases. Thus in order to compare the quality of the milk of any two quarters differences greater than .1 may be employed. The numbers set out in the lower

statement show the number of occasions on which the fore or hind-quarter was the richer.

Ingle made some tests on this point at Garforth in 1902.\* Samples were taken from each quarter of the udder of each of 19 cows, and it was found that the milk of the left fore-quarter of ten of these was poorer in solids-not-fat than from any of the other three quarters; in three cases it was poorer from the right hind-quarter; the other cases showed no characteristic differences. Ingle found however that a month later the left hind-quarter of one of the cows was poorest instead of the left fore-quarter. It is to be noted however that these tests included only *one* sample from each quarter, and bearing in mind the large experimental error which usually accompanies individual samples, no great weight can be attached to the record.

*Difference of % fat in morning and evening milk.*—In Statement VI the mean % fat in the morning and evening milk respectively for each sub-period and for each cow is set out. These percentages are derived from those in Statement III by taking the mean percentage of the left and right half-udders. Thus for cow Khaki, January, evening, 3.93 (Statement VI) is the arithmetic mean of 4.12 and 3.74 (*vide* Statement III) and for cow Subhagi, December, morning, 4.86 is the mean of 4.82 and 4.90. A cursory glance at the figures shows that the morning milk was for every cow richer than the evening, and even amongst the individual milkings it was very rare that this was not the case. In the last column of the statement the differences are set out. These vary a good deal; in some cases the difference is as small as .3%, but more generally it ranges from three-fourths to one and a half per cent. The mean difference for all the cows is .91% after weighting for differences of period. It is obviously far in excess of any experimental error.

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\* *Jour. Agr. Sci.*, I, 171.



*Statement VI.—Showing mean percentage of FAT in MORNING and EVENING milk respectively.*

Cow.	Month.	Morning Fat. %	Evening. Fat. %	Difference morning > evening.
Khaki ..	December ..	4.85	3.98	.87
	January ..	4.63	3.93	.70
Subhagi	December ..	4.86	4.02	.84
	January ..	4.87	4.05	.82
Amiri ..	December ..	4.55	3.89	.66
	January ..	4.61	3.87	.74
Kamali	April ..	4.80	3.46	1.34
	May ..	5.01	3.57	1.44
Nami ..	April ..	5.15	4.31	1.16
	May ..	5.48	4.60	.88
Radhi ..	April ..	4.77	3.64	1.13
	May ..	4.92	4.00	.92
Godhi ..	April ..	4.10	2.93	1.17
	May ..	4.16	2.97	1.19
Moghi ..	April ..	5.11	3.69	1.42
	May ..	5.15	3.77	1.38
Nathali	April ..	5.47	4.83	.64
	May ..	5.72	4.93	.79
Rami ..	April ..	4.03	3.72	.31
	May ..	4.76	3.99	.77
Janki ..	April ..	5.32	3.60	1.72
	May ..	5.19	3.81	1.38
Kaveri..	April ..	3.85	2.95	.90
	May ..	3.98	2.90	1.08
Giloni ..	April ..	4.14	2.80	1.34
	May ..	4.32	2.93	1.39
Boudhi	April ..	4.23	3.39	.84
	May ..	4.53	3.33	1.20
Gujri ..	April ..	5.44	4.08	1.36
	May ..	5.44	4.08	1.36
No. 160 Thoosri ..	September ..	5.30	4.25	1.05
	October ..	5.54	4.49	1.05
	November ..	5.28	4.61	.67
No. 130 Tikya ..	September ..	4.88	4.12	.76
	October ..	5.89	5.06	.83
	November ..	5.40	4.92	.48
No. 161 Mayani ..	September ..	3.93	3.29	.64
	October ..	4.73	4.30	.43
	November ..	5.50	5.08	.42



*Statement VI.—continued.*

Cow.	Month.	Morning Fat. %	Evening Fat. %	Difference morning > evening
No. 31 Balli .. {	September ..	4.83	3.74	1.09
	October ..	5.76	3.99	1.77
	November ..	5.55	4.22	1.33
No. 97 Kesari .. {	September ..	3.97	3.26	.71
	October ..	5.22	4.23	.99
	November ..	4.97	4.78	.19
No. 36 Gongli .. {	September ..	4.20	3.40	.80
	October ..	5.24	4.42	.82
	November ..	4.71	4.41	.30
No. 42 Chikni .. {	September ..	4.37	3.37	1.00
	October ..	5.16	3.81	1.35
	November ..	4.78	3.72	1.06
No. 56 Padmini .. {	September ..	4.86	4.09	.77
	October ..	5.74	5.21	.53
	November ..	5.92	5.45	.47
No. 50 Bhadki .. {	September ..	3.44	2.97	.47
	October ..	4.37	3.74	.63
	November ..	4.13	3.79	.34
No. 15 Hoosni .. {	September ..	3.64	3.14	.50
	October ..	4.30	3.45	.85
	November ..	3.93	3.60	.33

In England the difference in per cent. fat in morning and evening milk, when the periods between milkings are equal, is commonly a small one in favour of the morning milk.<sup>1</sup> At Poona, Meggitt and Mann<sup>2</sup> found that the evening milk of Gir and Sind cows was richer than that of the morning by approximately 1.0% fat. The periods of time which intervened between milkings at Poona were not, however, equal. Dr. Mann informs us that the cows were milked between 2 and 4 A.M. and between 12 noon and 2 P.M.; thus the periods may have been anything between 12 hours : 12 hours and 8 hours : 16 hours. The latter difference of period would account for a difference of 1.8% fat in favour of the evening milk, whilst if most of the periods were midway between the extremes, it would account for a difference of .8% fat. Messrs.

<sup>1</sup> S. H. Collins. *Proc. Univ. Durham, Phil. Soc.* 1911, IV, part 1.

<sup>2</sup> *Mem. Dept. Agri. Ind., Chem. Ser., Vol. II, No. 1, p. 36.*

Meggitt and Mann appear to have overlooked this influence in the % fat, and it remains an open question whether the Gir and Sind cows would not have yielded milk actually richer in the *morning* than in the evening if the periods between milkings had been equal.

Similarly, the tests which are quoted by Crowther<sup>1</sup> and in which the morning milk was found to be less rich than that of the midday or evening milking, do not provide very dependable evidence. At Garforth the intervals were equal, namely, 6 hours each, but this system was novel and was continued only for four days. At Offerton the intervals were 11, 8 and 5 hours.

Ingle's figures on this point are at variance with the general experience in England, but the average yield of milk after the 6-hour interval preceding 5 A.M. was so remarkable in the tests mentioned by him (40 lbs. as compared with 24 lbs. for other 6-hour intervals at Garforth) as to warrant an inference that the conditions were abnormal. The system of milking at 6-hour intervals was indeed novel, and continued only for four days, and it is not necessary to endorse Ingle's own suggestion, that the cows had become accustomed to produce richer milk in the day time by the long period during which they had been milked at the unequal intervals, in order to account for a difference in fat content, that, as his figures for absolute yield of fat show, is more than explained by the fact that for nervous or other reasons the cows yielded an excess of 66% of milk during the six hours preceding dawn.

There is of course abundant evidence to show that when the intervals between the milkings are very unequal, the quantity of milk given is usually greater and the fat % less after the longer interval. But that this is not always the case when the intervals are considerably less than 12 hours does seem to be shown by some of the figures obtained at Offerton with respect to cows milked three times in the 24 hours.

*Errors involved when milking in the ordinary way.*—The chief object of the tests which were made during Period C was to ascer-

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<sup>1</sup> *Jour. Agri. Sci.*, I, p. 154.

tain the errors which occur when cows are milked in the ordinary way. The method of experiment has been already detailed (page 151). It will be recollected that the ten cows were first milked for four weeks in September under the same conditions as in previous tests; they were then milked for four weeks as for profit; after which they were again milked for two weeks as in September.

*The yield of milk.*—The mean yield of milk is set out in Statement VII for each of the ten cows, together with the error,  $r_o$ , of the mean. In Statement VIII are set out the values of the probable error  $r$  of the individual milking.

*Statement VII.—Showing the mean YIELDS of milk during PERIOD C.*

Cow.	SEPTEMBER 28 DAYS.		OCTR. 28 DAYS.		NOVEMBER 14 DAYS.	
	Left side. lbs. $r_o$	Right side. lbs. $r_o$	lbs. $r_o$		Left side. lbs. $r_o$	Right side. lbs. $r_o$
No. 160 Thoosri ..	3.60 $\pm$ .06	3.64 $\pm$ .06	5.14 $\pm$ .07		2.68 $\pm$ .09	2.11 $\pm$ .14
No. 130 Tikya ..	4.06 $\pm$ .04	4.00 $\pm$ .02	7.06 $\pm$ .09		4.11 $\pm$ .08	3.71 $\pm$ .07
No. 161 Mayani ..	5.42 $\pm$ .06	5.52 $\pm$ .08	8.56 $\pm$ .06		4.89 $\pm$ .19	5.18 $\pm$ .11
No. 31 Balli ..	6.08 $\pm$ .04	6.09 $\pm$ .04	9.26 $\pm$ .13		4.32 $\pm$ .07	4.46 $\pm$ .14
No. 97 Kesari ..	6.21 $\pm$ .05	6.09 $\pm$ .07	9.39 $\pm$ .11		4.75 $\pm$ .07	4.75 $\pm$ .06
No. 36 Gongli ..	6.23 $\pm$ .04	6.20 $\pm$ .04	10.72 $\pm$ .09		5.89 $\pm$ .05	5.86 $\pm$ .05
No. 42 Chikni ..	7.67 $\pm$ .07	7.61 $\pm$ .06	10.54 $\pm$ .16		4.82 $\pm$ .11	5.25 $\pm$ .15
No. 56 Padmini ..	8.27 $\pm$ .07	8.36 $\pm$ .08	13.25 $\pm$ .18		6.11 $\pm$ .07	6.43 $\pm$ .08
No. 50 Bhadki ..	9.90 $\pm$ .08	9.84 $\pm$ .08	15.45 $\pm$ .20		8.32 $\pm$ .07	8.11 $\pm$ .12
No. 15 Hoosni ..	11.73 $\pm$ .16	11.80 $\pm$ .15	17.22 $\pm$ .30		8.82 $\pm$ .12	8.71 $\pm$ .25

*Statement VIII.—Showing the values of the probable error,  $r$ , for individual milkings during Period C.*

Cow.	SEPTEMBER (28 DAYS).		OCTOBER (28 DAYS).	NOVEMBER (14 DAYS).	
	Left side. $r$	Right side. $r$		Left side. $r$	Right side. $r$
No. 160 Thoosri ..	$\pm$ .22	$\pm$ .23	$\pm$ .40	$\pm$ .25	$\pm$ .37
No. 130 Tikya ..	$\pm$ .14	$\pm$ .07	$\pm$ .47	$\pm$ .21	$\pm$ .18
No. 161 Mayani ..	$\pm$ .23	$\pm$ .29	$\pm$ .33	$\pm$ .50	$\pm$ .29
No. 31 Balli ..	$\pm$ .14	$\pm$ .16	$\pm$ .67	$\pm$ .19	$\pm$ .38
No. 97 Kesari ..	$\pm$ .17	$\pm$ .28	$\pm$ .59	$\pm$ .19	$\pm$ .17
No. 36 Gongli ..	$\pm$ .14	$\pm$ .16	$\pm$ .47	$\pm$ .15	$\pm$ .13
No. 42 Chikni ..	$\pm$ .27	$\pm$ .23	$\pm$ .87	$\pm$ .29	$\pm$ .39
No. 56 Padmini ..	$\pm$ .24	$\pm$ .32	$\pm$ .95	$\pm$ .19	$\pm$ .21
No. 50 Bhadki ..	$\pm$ .29	$\pm$ .31	$\pm$ 1.05	$\pm$ .19	$\pm$ .30
No. 15 Hoosni ..	$\pm$ .56	$\pm$ .55	$\pm$ 1.60	$\pm$ .32	$\pm$ .67

The reliability of these tests is more perfectly judged from the values of  $r$  in Statement VIII than from those of the probable error of the mean  $r_0$  in Statement VII, because the former is not so seriously affected by the difference of length of the periods. The values of the probable error are very similar for the sub-periods  $C_1$  and  $C_3$  respectively, those of  $C_3$  being somewhat the greater. Compared with sub-period  $C_2$ , they are for nine cows out of the ten, very much smaller, being only about one-third as great. Thus the effect of hand-milking in the ordinary way when the calf takes an indefinite amount of milk, is to yield results which are open to a very much larger experimental error than when the portion taken by the calf is controlled in the manner which was adopted during the major part of these trials.

Referring to the probable error of the mean,  $r_0$ , of Statement VII, it must be recollected that this is, for September or November, derived from only one-half and one-quarter respectively the number of milkings on each side of the udder, as of milkings in October, which explains why the differences between the several values are not so great as those of the probable error,  $r$ , of Statement VIII.

The actual yields of milk are of less importance in this respect. They varied within much wider limits than did those of Periods A and B.

*The amount of milk taken by the calf.*—It has been shown (p. 153) that during the periods when the one-half of the udder was sucked, the calf must have taken one-half the total milk. It is therefore possible to form an estimate of how much the calf took during October on the assumption that the production during this month was the mean of that of the preceding and succeeding months. This information is set out in the subjoined Statement IX.

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*Statement IX.—Showing the amount of MILK taken by the CALF.*

Cow.			Weighted mean total produc- tion per day during sub- periods C <sub>1</sub> & C <sub>2</sub>	Mean yield by hand per day during sub-period C <sub>2</sub>	Difference taken by calf daily during sub-period C <sub>2</sub>	Portion taken by calf daily during sub- periods C <sub>1</sub> & C <sub>2</sub>
			lbs.	lbs.	lbs.	lbs.
Thoosri	..	..	6.42	5.14	1.28	3.21
Tikya	..	..	7.98	7.06	.92	3.99
Mayani	..	..	10.65	8.56	2.09	5.33
Balli	..	..	11.04	9.26	1.78	5.52
Kesari	..	..	11.37	9.39	1.98	5.68
Gongli	..	..	12.20	10.72	1.48	6.10
Chikni	..	..	13.54	10.54	3.00	6.77
Padmini	..	..	15.27	13.25	2.02	7.63
Bhadki	..	..	18.64	15.45	3.19	9.32
Hoosni	..	..	21.53	17.22	4.31	10.76

A consideration of the last two columns of this statement shows that the calf had about one-third as much milk during October when the cow was milked for profit, as during the other sub-periods.

*Effect of meteorological conditions.*—It is generally considered that milch-cows are commonly affected by changes in the weather, which is reflected in either yield or quality of the milk, or both. Assuming that this is so, it *might* be a chief contributory cause of the comparatively large error which we have found in yield and quality for any one milking. In that case comparison of daily meteorological data with the milk data should show a defined correlation between cause and effect. Our tests were not designed with a view to tracing such a correlation; and hence we are not in a position to make it thoroughly. At the same time we have, as a matter of fact, compared the daily milk data with the meteorological data and have failed to trace any definite connection.

*Analysis of Montgomery cattle milk.*—This memoir would be incomplete if some examples of the more complete analyses of the milk of this herd were not quoted; these are set out in the accompanying Statement X.



Statement X.—Showing the composition of the milk of each cow.

	PERIOD A.			PERIOD B.											
	Khaki.	Subhagi.	Amiri.	Kamali.	Nami.	Radhi.	Godhi.	Moghi.	Nathadi.	Rami.	Janki.	Kaveri.	Gilori.	Boulhi.	Gujri.
	No. 51.	No. 88.	No. 91.	No. 159.	No. 128.	No. 101.	No. 99.	No. 44.	No. 67.	No. 78.	No. 95.	No. 183.	No. 85.	No. 33.	No. 30.
Fat % ..	4.40	4.59	4.45	5.10	5.52	4.50	3.70	4.40	5.45	4.70	4.55	4.45	3.95	4.35	5.15
Solids-not-fat	8.25	8.46	8.33	8.66	9.31	9.00	8.26	8.71	8.85	8.42	8.44	8.56	8.18	8.50	8.28
Total solids %	12.65	13.05	12.78	13.76	14.83	13.50	11.96	13.11	14.20	13.12	12.99	13.01	12.13	12.85	13.43
Sp. gr. ..	1029	1029	1028	1029	1030	1031	1029	1031	1031	1029	1030	1029	1029	1028	1026

PERIOD C.										
	Thosari.	Tikya.	Mayani	Balli.	Kesari.	Gongli.	Chikni.	Padmini.	Bhadki.	Hoosni.
	No. 160.	No. 130.	No. 161.	No. 31.	No. 97.	No. 36.	No. 42.	No. 56.	No. 50.	No. 15.
Fat % ..	5.42	5.20	4.32	4.50	4.40	4.62	4.39	5.21	3.53	3.39
Solids-not-fat ..	8.90	8.67	8.05	8.47	8.30	8.22	8.16	8.35	7.53	8.21
Total solids % ..	14.32	13.87	12.37	12.97	12.70	12.84	12.55	13.56	11.06	11.60
Sp. gr. ..	1030	1029	1028	1030	1029	1028	1028	1028	1028	1030

## GENERAL CONCLUSIONS.

Although the initial object in view, when it was decided to keep a series of special records of the milk of the Montgomery herd at Pusa, was to ascertain its average yield and quality, the primary object almost immediately became a check on the *errors of experiment* which occur in obtaining such records. It has thus happened that throughout the work the mind has been concentrated on these errors rather than on the actual yield and fat percentage, although the latter were at the same time ascertained.

Of the two chief known sources of error, that due to *difference of period between milkings* can be readily extinguished by making the periods equal, and this presents no difficulties. The other, namely, the *error due to the calf sucking* while the cow is hand-milked, has been overcome by the simple arrangement of allowing it to suck the one half udder only whilst the other half is entirely hand-

milked. This procedure has presented no difficulties, and for such cows as the Montgomery breed at Pusa the data show very definitely that the calf actually took one-half of the milk. The question was naturally raised as to whether this would be so in all cases, but there is no doubt that even with those cows whose total yields were the largest (for example, cow Hoosni, 21 lbs. per day), the calf took the half during September and November.

In estimating the magnitude of the error which would occur if milk yields are estimated by simply milking as for profit when the calf takes an unknown quantity, the value of the probable error,  $r$ , shows that this is at any rate three times as great as it is if the calf is allowed the whole of the milk from one side of the udder. Thus it is evident that the procedure we have adopted reduces the error in estimating milk yields under Indian conditions very much indeed.

The probable error in the estimation of the % fat in individual samples we have found to be about  $\pm 3$ . It is of interest to compare this with such other similar data as are obtainable from published records, although the latter are not strictly comparable chiefly because the records are not for consecutive days. Those published by Meggitt and Mann<sup>1</sup> refer only to single samples taken once a week (on Fridays), although at first sight the figures appear as averages for the week. The probable error for some of these cows is as follows:—

					A.M.	P.M.
Gir No. 1	..	..	..	..	5.48 $\pm$ .66	6.41 $\pm$ .72
" " 3	..	..	..	..	4.29 $\pm$ .38	4.80 $\pm$ .18
" " 4	..	..	..	..	4.77 $\pm$ .44	5.50 $\pm$ .60
" " 5	..	..	..	..	4.82 $\pm$ .23	5.80 $\pm$ .63

It is at once apparent how much smaller was the error at Pusa when the calf was restricted to the one half udder. The errors which accompanied the Poona tests are indeed very similar to those relating to yield which occurred at Pusa in October 1912

<sup>1</sup> *Mem. Dep. Agr. Ind., Chem. Ser., Vol. II, No. 1.*

when the calf took an unknown quantity of milk (*vide* Statement VIII, page 168). Some other records published by the Durham County Council<sup>1</sup> showed the following errors:—

				A.M.	P.M.
Cow No.	3	..	..	3.62 ± .32	4.08 ± .28
" "	5	..	..	3.90 ± .54	3.93 ± .51
" "	6	..	..	4.01 ± .37	4.72 ± .47

The *required number of tests* of any one cow in order to obtain a mean value of % fat within certain limits may be judged from these records. It will naturally depend on the degree of exactitude required, but it is evident that when 14 or 15 tests are made, as for example from either side of the udder during April and May, the value of  $r_0$  for % fat was in the neighbourhood of  $\pm .1$ . This is equivalent to a probability of about 24 : 1 that the experimental error does not exceed .3% fat. If therefore such a degree of exactitude is not considered sufficient, the number of tests would have to be increased very considerably in order to reduce the error materially.

Regarding the maximum *yield* of milk of cows of this herd per day this may be said to vary for different cows, from 7 to 20 lbs. Among the greater number of the cows the variation was not nearly so great and about 12 lbs. may be said to be an average figure. It is to be recollected that this is the maximum *production*; when milking in the ordinary way for profit the calf had about 2 lbs. of this, leaving some 10 lbs. as the average maximum yield to the milkman.

Information regarding the yields of other Indian breeds is comparatively scarce. Details for Gir and Sind cows are given by Meggitt and Mann, but it is quite uncertain how much the calf took. On the days when the samples were taken, once a week the calf was allowed "as little as possible," but presumably the yields which are quoted refer to the actuals, all days included,

obtained in practical dairying. In that case the circumstances would be comparable with those of our period C<sub>2</sub>, October 1912. The average yield for Gir cows per head per day was found to be about 6 lbs. and for Sind cows about 10 lbs.; if to these be added some 2—4 lbs. probably taken by the calf, the sum would indicate a total production of milk similar to that which we have found for the Montgomery breed. The estimate is obviously only a very rough one, but it is the best that one can make. In comparison with European cattle it is hardly necessary to point out that such yields fall far short of an European average. Even Jersey cattle will commonly yield a maximum of 25 lbs. and breeds like the Shorthorn 35 lbs. in the day.

*In respect of richness* Indian cows' milk has generally been found to contain a higher percentage of fat than that of most European cattle. Among the Montgomery cattle which were included in our tests, the % fat varied from about 3.5 to 5.0. This is less than what Meggitt and Mann found in the milk of the two breeds at Poona; the milk of the Gir cows contained from 5.0 to 6.0%, that of the Sind cows from 5.0 to 6.5%. But the fact of the calf drawing an unknown quantity of the first and poorer milk in those tests would naturally increase the % fat in the remainder.

Our mode of experiment has enabled us to draw certain conclusions regarding the *yield and quality of the milk from the several parts of the udder*. Certain of the cows appeared to yield rather more milk from one side of the udder than from the other; altogether there were five such instances among 25 cows. On the whole however the experiments have shown that that obtained from opposite sides is, as indeed would be expected, generally similar both in quantity and quality. But it is less in accordance with expectation that the milk from the fore and hind-quarters should have been found to differ very greatly, not only as is commonly observed, in quantity, but also in quality. The tests of the milk from the several quarters of the udder of three cows indicated that there are differences in quality characteristic of the cow;

one cow yielded milk from the fore-quarter which was systematically richer than that from the hind-quarter, whilst another yielded richer milk from the hind than from the fore-quarter; the third cow showed no such characteristic differences. Generally then the conclusion must be drawn that characteristic differences both of yield and of quality of milk from the fore and hind-quarters of the udder of cows may commonly occur. Taken in conjunction with the uniformity of composition of the whole milk of individual cows, this would seem to indicate that the quality of the milk is a function of the tissue of that region of the cow's udder in which it is produced and that though the opposite sides are symmetrical in this respect, the udder is in other directions no more uniform in function than it is in shape.

This conclusion is in accordance with those drawn by Ingle ;\* though he found that in respect of the percentage of solids-not-fat, the milk from corresponding quarters of opposite sides of the udder differed very considerably and erratically.

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\* *Highland and Agric. Soc. Trans.* 1903, XV, 135.





# THE SYSTEM POTASSIUM NITRATE, SODIUM CHLORIDE, WATER.

BY

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## INTRODUCTION.

DURING the last two years attempts have been made by us to improve the methods of refining saltpetre in India. This subject was dealt with in *Bulletin* No. 24 of the Agricultural Research Institute, Pusa, and it is merely necessary to mention here that the crude material consists of a mixture of potassium nitrate, sodium chloride and mud, together with small amounts of other salts, such as sodium nitrate, potassium chloride, magnesium sulphate, etc. The refining process as carried out in India consists simply in the solution of the nitrate in hot water or hot mother liquor, separation of the mud by sedimentation, and crystallisation of the nitrate from the cleared liquor as it cools.

It was of importance for our purpose to possess information regarding the solubility of potassium nitrate in the mother liquors and in presence of excess of sodium chloride at temperatures near the boiling point, as also to know in how far the concentration of potassium nitrate in solution at these high temperatures would affect the composition of the liquid phase and that of the crystallised mixture of salts obtained on cooling.

Although the production of potassium nitrate from sodium nitrate and potassium chloride is an industry which is carried on on a fairly large manufacturing scale, an examination of the literature showed that the information regarding this system is both limited and very defective.

For a full appreciation of it, information of all the following systems is required :—

- (i) Potassium nitrate, water
- (ii) Potassium chloride, water
- (iii) Sodium nitrate, water
- (iv) Sodium chloride, water
- (v) Potassium nitrate, Sodium nitrate, water
- (vi) Sodium nitrate, Sodium chloride, water
- (vii) Sodium chloride, Potassium chloride, water
- (viii) Potassium chloride, Potassium nitrate, water
- (ix) Potassium nitrate, Sodium chloride or Sodium nitrate, Potassium chloride, water

at temperatures varying from 20°C. to 100°C. Of these full data regarding Nos. *i*, *ii*, *iii* and *iv* are available. Data for system *v* have been published by Carnelly and Thomson<sup>1</sup> at 20°C. For system *vi* some data have been published at 15°C. by Bodlander,<sup>2</sup> at 20°C. by Nicol.<sup>3</sup> For system *vii* data have been published by Nicol<sup>4</sup> at 20°C., and by Precht and Wittgen,<sup>5</sup> Soch<sup>6</sup> and Etard<sup>7</sup> for various temperatures from 0°—100°C. For system *viii* some data have been published for temperatures 14.5° and 25.2°C. by Touren,<sup>8</sup> by Bodlander<sup>9</sup> for temperature 17.5°C., and by Nicol<sup>10</sup>

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<sup>1</sup> *Journ. Chem. Soc.*, 1888, 53, 799.

<sup>2</sup> *Physik. Chemie.* 1891, 7, 361.

<sup>3</sup> *Phil. Mag.* (5) 31, 369.

<sup>4</sup> *Phil. Mag.* 1891, 31, 369.

<sup>5</sup> *Ber.* 14, 1667.

<sup>6</sup> *Journ. Physic. Chem.* 1898, 2, 46.

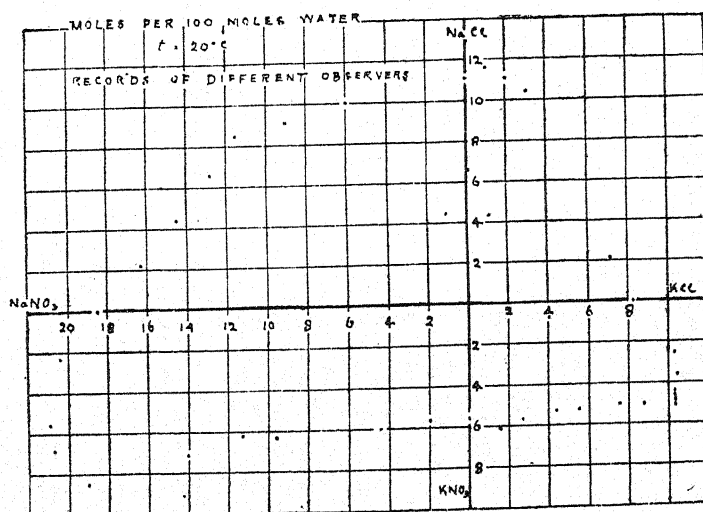
<sup>7</sup> *Ann.-Chim. Phys.* (7) 3, 375.

<sup>8</sup> *Compt. Rend.* 130, 908.

<sup>9</sup> *Physik. Chem.* 1901, 7, 360.

<sup>10</sup> *Phil. Mag.* 1891, 31, 369.

for temperatures  $20^{\circ}$ ,  $25^{\circ}$  and  $80^{\circ}$ . Finally for system *ix* some data have been published by Etard,<sup>1</sup> but since at full saturation three salts must be present and he only mentions two, it is evident that this information is imperfect; there is also a collection of data by Kenjiro Vyeda-Kyoto<sup>2</sup> for  $25^{\circ}\text{C}$ . These various data are not only mostly restricted to certain specified temperatures, but also when plotted as in chart No. 1 for temperature  $20^{\circ}\text{C}$ . they disagree considerably among themselves.

CHART N<sup>o</sup> 1

It was evident then that each of the systems *v* to *viii* must be worked out for temperatures such as we had to employ in the refining process, as well as system No. *ix*. This has been completed for temperatures  $20^{\circ}$ ,  $30^{\circ}$ ,  $40^{\circ}$  and  $91^{\circ}$ .

### EXPERIMENTAL.

Before considering the data obtained it is necessary to explain  
(i) the mode which we have adopted in order to obtain equilibrium,  
(ii) our method of securing a suitable specimen which we believe to be novel, and (iii) the mode of analysis and deductions therefrom.

<sup>1</sup> *Ann.-Chem. Phys.* (7) 3, 283.

<sup>2</sup> *Mem. Coll. Sci. Eng. Kyoto Imp. Univ.* 1910.

(*Zeits. für anorg. Chem.* 1911, LXXI, 1).

*Attainment of Equilibrium.*

The mode of obtaining the saturated solution in any experiment was practically that described by Meyerhofer and Saunders.<sup>1</sup> The quantities of water and salt or salts are weighed in a cylindrical glass tube, measuring  $7'' \times 1\frac{1}{2}''$ , which was fitted with a stopper and stirring paddle. The mixture was then heated to a temperature above that at which equilibrium was to be attained. Hence we always started with a more concentrated solution and the excess of salt allowed to crystallise out. This procedure was adopted principally because the quantities of salt before solution were in many cases so very great compared with the water, that it was difficult to keep the paddle moving at all. Even with the above procedure, the excess quantities of salts at high temperatures such as  $90^{\circ}\text{C}$ . are sufficient to cause a material resistance to the paddle. The glass cylinder was fixed vertically in a water-bath and motion was given to the paddle from a small hot-air engine. The water in the bath was also maintained in motion continuously by a paddle and its temperature was controlled by a Novy's regulator.

For temperatures up to  $40^{\circ}\text{C}$ . no difficulty was experienced in maintaining the temperature constant within  $0.2^{\circ}\text{C}$ .; at the higher temperature  $91^{\circ}\text{C}$ ., the considerable and constantly varying rates of evaporation from the bath were avoided by covering the water surface with a layer of paraffin wax, when the variation of temperature fell to  $0.2^{\circ}\text{C}$ .

The *time required* for attainment of equilibrium we found to be less than 18 hours. The procedure was to weigh off the materials at about 11 o'clock; the mixture was then agitated constantly in the bath until 7 o'clock on the following day when a sample of the clear solution was withdrawn; the agitation was then again continued until 10 o'clock when a second specimen was taken.

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<sup>1</sup> *Zeits. f. Phys. Chem.* XXVIII, 451.

The following examples show that equilibrium had set in at the time the first sample was taken.

System.	First sample.			Second sample taken 3 hours later.		
	Moles per 100 moles H <sub>2</sub> O.					
	NaNO <sub>3</sub>	NaCl.	KCl.	NaNO <sub>3</sub>	NaCl.	KCl.
NaNO <sub>3</sub> +NaCl. t = 20°C	12.20	6.42	..	12.36	6.43	..
NaCl+KCl. t = 0°C ..	..	9.92	2.40	..	10.12	2.25

In addition to this knowledge of the time required for equilibrium to set in, the charting of the data provides a second indication of the correctness or otherwise of any particular experiment. As will be seen, these lie very uniformly indeed on the curves and very few of the second samples had to be analysed.

The examination of any system was made as follows:— Suitable quantities of water and one of the two salts, A, were weighed off in the cylinder, the quantity of salt A being sufficient to provide an excess over that which would pass into solution. After attaining equilibrium (on the following day) specimens were taken in the manner subsequently described. The reaction tube was now weighed and a suitable portion of the second salt B added, this portion being estimated as probably about one-fourth part of the total which would dissolve in the presence of salt A. The reaction tube was replaced in the bath, and after equilibrium was attained specimens of the solution were withdrawn. The reaction tube was weighed and another fraction of salt B was added. Thus day by day the solutions of the system containing excess of A plus increasing portions of B were prepared until an excess of B also was present.

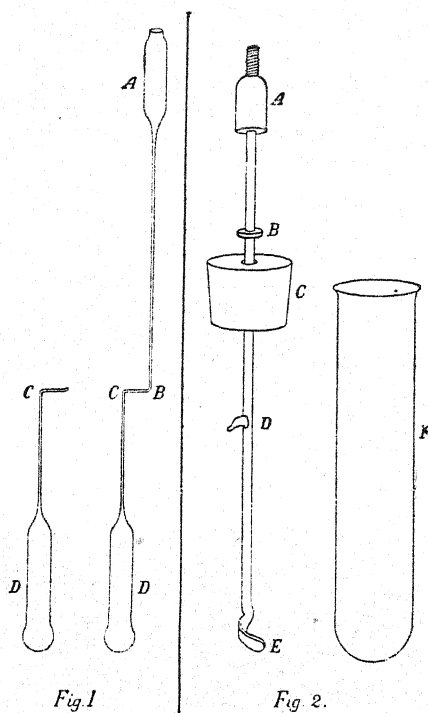
*Taking a specimen of the solution.*

Various devices have been adopted for taking a specimen of a saturated solution. We desired to determine not only the com-

position of the solutions but also the specific gravity if possible, and consequently it was necessary to take a known weight and volume of clear solution from the reaction vessel. None of the various forms of apparatus which have been published by others was quite suitable, more especially at the higher temperatures. Van't Hoff's tapped pipette, which has been employed at temperatures not far removed from that of the room, is quite unsuited to the case where the variation of so little as  $1^{\circ}\text{C}.$  in temperature causes serious precipitation of dissolved substance. We therefore devised a glass tube which promised to remove errors more perfectly than other known apparatus, and which is illustrated by Fig. 1. A piece of rather thin walled glass tube of about 1 cm. diameter is blown round at one end and drawn out to a stout long capillary at the other; it is then cut off at the open end. The portion D is about 6 cm. long and A is some 4 — 5 cm. long. The capillary is then bent to a right angle at B and C, the length of capillary from C to tube D being about 5—6 cm. The tube A, B, C, D is now attached to a good exhaust pump and the air removed as far as possible. For our work, the pressure was reduced to 1.5 or 2.0 mm. In any case it is of importance, if the volume of the specimen is to be subsequently ascertained, that this exhaustion shall be good. Having thus reduced the pressure in D, the capillary is sealed off at B and there remains the exhausted portion C D. The volume of this tube has usually been about 3 to 5 c.c. for our work. When it is desired to take a specimen from the reaction tube F (see Fig. 2) the rotation of the paddle A, B, D, E is stopped and the salts allowed to settle which takes place very quickly. A scratch is now made on the *inside* of the right angle of the capillary at C. The tube C D is then inserted capillary downwards into the reaction fluid in F and the bent part of the capillary is brought under the hook D on the paddle stem; by pressing the exhausted tube carefully upwards, the piece of capillary is broken off and the liquid runs up and nearly fills the tube C D. This takes place naturally very quickly (in about half a second) and the operator removes the tube from the reaction



fluid; the capillary is immediately wiped clean on the outside. At high temperatures the tube was protected by a cloth wrapping

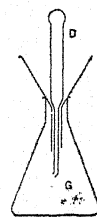


to prevent it partially from cooling. There is thus obtained a tube nearly full of the liquid, the temperature of which could only alter slightly before it was removed from the reaction vessel and the adhering liquid wiped off. So far as composition *by weight* is concerned, it was a perfect specimen. In respect of volume, an error lay in the fact that the specimen tube contained some air, and that the volume of this would be increased by the vapour of the liquid. The volume of the tube had also to be ascertained.

*Removal of the specimen from the tube.*

Immediately after taking the specimen it was weighed if approximately at room temperature, or as soon as it cooled sufficiently if originally hot. No protecting cap was placed over the open capillary mouth, because the error due to evaporation before

weighing was found to be negligibly small (less than .5 milligram). The tube was then placed, capillary downwards, in a funnel which was supported over an Erlenmeyer flask, and this combination of apparatus was then placed in an otherwise empty vacuum desiccator. On reducing the pressure, the liquid ran out of specimen tube D into the flask G. In the case of the solutions saturated at high temperature, such as  $91^{\circ}\text{C}.$ , the liquid on cooling in the specimen tube became so solid that the small amount of mother liquor could not pass through the capillary, and these tubes were therefore placed capillary downwards in a small vessel of water in an air-oven for some hours. Some of the warmed liquid then passed out of and some water passed into the specimen tube so that the latter could now be partly emptied by exhaustion in the vacuum desiccator. In either case the result of the first exhaustion in the desiccator is to remove a part of the reaction fluid and salts from the specimen tube; the whole must of course be removed. The desiccator is opened, and the specimen tube placed, capillary downwards, in a small beaker of water, which is placed in the vacuum desiccator; the air is pumped out which also partly exhausts the specimen tube; on re-admitting air to the desiccator, water passes from the beaker into the specimen tube. The latter is taken out, shaken carefully, replaced on the arrangement of funnel and flask in the desiccator; the latter is exhausted which causes the wash fluid to run out. By alternately allowing water to flow into the specimen tube, shaking and removing it again about five times, the whole of the original contents of the tube were transferred in a diluted state to the Erlenmeyer flask.



It was now necessary to ascertain (i) the weight of the dry specimen tube, (ii) its volume.

*Ascertaining the volume of the tube.*—The washed tube was placed, capillary downwards, in a small beaker of distilled water, then placed in a vacuum desiccator and the pressure reduced

to what it had been when the tube was first prepared; air was now admitted, when the tube became filled with water. The error due to residual air will be dealt with presently. The tube is next placed capillary upwards in a beaker of water at room temperature and allowed to assume the temperature of this water, for the temperature of the water with which it is filled, is, owing to the accelerated evaporation in the vacuum, very much below the room temperature. The tube is then wiped dry and weighed.

*Drying the tube.*—The weight of the dry tube must now be ascertained. For this purpose the water is taken out of it in the vacuum desiccator and the tube must now be dried perfectly. The following method was employed which is very rapid and perfect. The wet specimen tube is placed in a stout tube (shaped as a test tube) and joined to one inlet of a *large* calcium chloride tube; the latter is connected from the outlet to a three-way tapped tube, which again is connected to the pump. On exhausting the apparatus the damp air from the specimen tube and its encasing tube is brought into the calcium chloride tube where it becomes dried. After attaining a good vacuum, the three-way tap is turned so as to admit air from the room into the calcium chloride tube, which causes dried air to flow into the encasing tube and specimen tube. This dried air immediately takes up water from that in the specimen tube. It follows that by alternately pumping out the damp air and re-admitting dried air, the water originally in the specimen tube becomes vapourised and entirely removed. The process is quite rapid; the change in weight of the specimen tube after the fourth or fifth exhaustion being less than .1 milligram. There have now been obtained the following data:—

- (a) weight of dry specimen tube,
- (b) weight of tube filled with water at known temperature,
- (c) weight of tube filled with reaction liquid at known temperature.

Of these :—(a) is correct. (b) and (c) are subject to error due to the fact that in neither case is the tube actually filled with the liquid. This error can however be calculated with sufficient precision, as follows :—

Let  $x$  be the volume of the tube as ascertained under (b). This is too small by the volume of the damp air which was left in by the pump. Let the pressure registered by the manometer =  $p$ . The volume of air *originally* left in the tube will be  $V_{(A)} = \frac{x p}{760}$  (approximately).

When the tube is filled with water or solution, the volume of the residual air will be increased by the water vapour and will be (approximately)  $V_{(A+W)} = V_{(A)} \frac{760}{760 - T} \times \frac{1 + \alpha t}{1}$

The atmospheric pressure may be assumed to be 76 cms. for these calculations.  $T$  = Vapour pressure.

In our work no correction in the volume of the salt solution as ascertained from the weight of water which the tube contained at 20° and 30° was necessary, as the difference is negligibly small. For the higher temperatures 40° and 91°C. the following were the corrections :—

At 40° C. *deduct* .0027 c.c. for each 5 c.c. apparent volume.

At 91° C. *deduct* .0431 c.c. for each 5 c.c. apparent volume.

The vapour pressure of the salt solutions has been assumed to be identical with that of water. This is admittedly not actually the case, but the published information on the subject is too slight to admit of a more exact correction.

The foregoing procedure has thus provided :—

- (i) weight of the specimen of saturated solution;
- (ii) its volume, at the temperature of equilibrium, within an error at 91° C. of less than .01 c.c. in 5 c.c. which is equivalent to an error of about .005 in the specific gravity. At the lower temperatures this error is negligibly small.

*Analysis of the solution.*—Reference to the analysis of the solution is only necessary in the following respects.

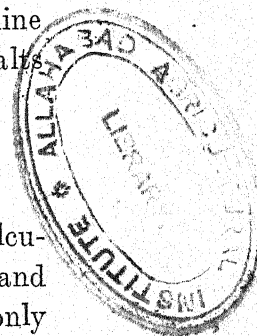
(i) *The analysis of known fractions* was naturally necessary.

To this end the weight of the small Erlenmeyer flask, into which the contents of the specimen tube were washed, was previously ascertained and the weight of total solution subsequently. The contents were carefully mixed by agitation; the lip was greased, and portions poured out into suitable vessels, the weights of which were obtained by difference.

(ii) In cases where the solution contained only one salt, the quantity of this could be ascertained from either the weight of total residue or from a determination of one constituent. Usually the former was employed. Where two salts were present, at least two items must be determined, but a third was also often made thus:—for system (v)  $\text{KNO}_3 + \text{NaNO}_3$ , the total salts and potassium were determined in all cases and the  $\text{NO}_3$  in some cases. It is better to determine that constituent which occurs in one of the salts rather than one which occurs in both.

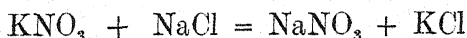
*The determination of the solid phases.*

The nature of the solid phases can be very definitely calculated from the known weight of salts and water initially taken and the subsequently ascertained concentrations of solution; the only source of error, apart from those of analysis, being the loss of water from the reaction vessel during the 20 hours or so of agitation, for it is clear that in order to ascertain from the analysis of the specimen, the weight of total salt or salts in solution, an equally accurate knowledge of the quantity of water in the reaction vessel at the end of the period of agitation is necessary. It was therefore important to reduce the loss due to evaporation of water from the reaction vessel to such small limits that it could be estimated.



For temperatures 20°, 30° and 40° the reaction vessel was covered by a rubber cap. At these temperatures the loss of water amounted to .6 gm. at 30° and to 2.1 grms at 40° per 20 hours. For the temperature 91° the reaction vessel was closed by a rubber stopper (Fig. 2) and the loss of water amounted to only 1.5 gm. for the same period. These quantities although not negligibly small, are sufficiently well defined to admit of the necessary correction.

Where two salts with a common ion were present no doubt exists as to the solid phase or phases, but where the two salts do not contain a common ion, such as in system (ix)



it is evident that it is a four component system (including water) and that an excess of both salts will necessitate the presence of three solid phases. There may however be only one, or two solid phases present with an unsaturated solution. The case is so far simplified in that no known hydrates of any of these salts exist at temperatures between 20° and 100° C. The decision as to the third salt in solution, is readily provided by the analytical data as explained in the preceding para.

*The data obtained.*

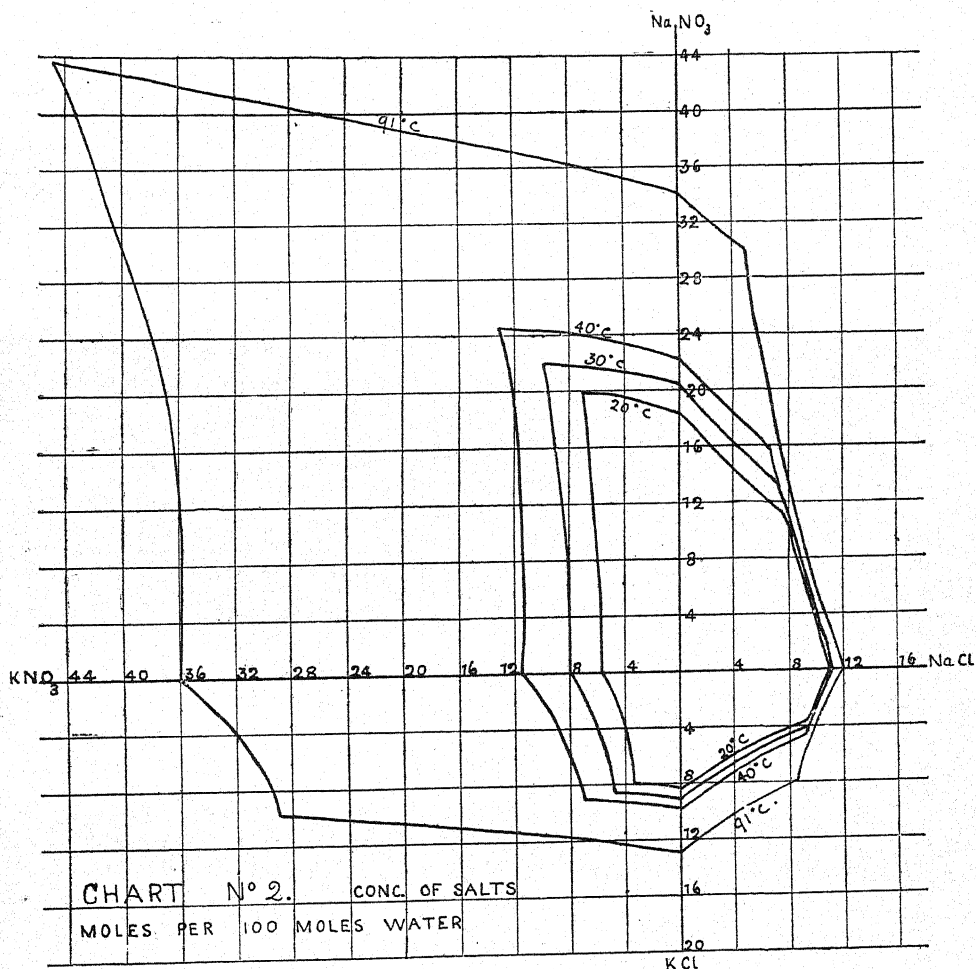
The data obtained are set out in the following five statements, each of which deals with one of the five systems at the temperatures 20°, 30°, 40° and 91° C. For each temperature there are two sets of data, referring respectively to the gradual addition of quantities of the one salt A to a saturated solution of B, and the addition of B to saturated solution of A. The data include the following :—

- (i) the actual quantities of salts and water which were placed in the reaction vessel, and
- (ii) the same after equilibrium, distributed in the liquid and solid phases ;



(iii) the concentration of the solutions expressed as (a) grms. per 100 grms. water, (b) moles per 100 moles water, (c) grms. per 100 c.c. solution;

(iv) the specific gravity of the solution, this being simply the ratio  $\frac{\text{weight}}{\text{volume}}$  at the specified temperature.



The above chart No. 2 shows the concentrations (moles per 100 moles water) of the solutions.

STATE

*The system*

System.	MATERIALS IN REACTION VESSEL.						
	Initially added.			AT EQUILIBRIUM.			
				In solution.		Solid phases.	
	KCl grms.	NaCl grms.	H <sub>2</sub> O grms.	KCl grms.	NaCl grms.	KCl grms.	NaCl grms.
<i>Temperature</i>							
KCl ..	54.00	..	141.9	49.12	..	5.88	..
KCl + NaCl (1) ..	51.92	13.80	135.7	36.10	13.75	15.82	..
KCl + NaCl (2) ..	50.47	26.60	129.1	25.37	26.30	25.10	..
KCl + NaCl (3) ..	49.40	37.89	123.2	18.38	37.40	31.02	0.49
KCl + NaCl (4) ..	48.73	48.53	131.8	20.24	39.03	27.49	9.50
NaCl ..	..	56.00	138.7	..	49.41	..	6.59
NaCl + KCl (1) ..	13.20	54.19	132.7	12.90	43.00	..	11.19
NaCl + KCl (2) ..	25.63	52.62	127.3	18.80	38.66	6.83	13.96
NaCl + KCl (3) ..	..	..	..	..	..	..	..
<i>Temperature</i>							
KCl ..	57.20	..	140.9	52.95	..	4.25	..
KCl + NaCl (1) ..	56.00	14.00	138.9	40.91	14.07	15.09	..
KCl + NaCl (2) ..	54.66	26.54	132.6	30.27	26.41	24.39	..
KCl + NaCl (3) ..	53.66	36.68	127.3	21.39	37.41	32.27	..
KCl + NaCl (4) ..	53.04	45.62	121.7	20.51	36.58	32.53	9.04
NaCl ..	..	53.00	128.4	..	46.64	..	6.36
NaCl + KCl (1) ..	14.00	51.90	141.5	14.08	45.64	..	6.26
NaCl + KCl (2) ..	26.53	50.38	135.7	22.30	41.40	4.23	8.98
NaCl + KCl (3) ..	..	..	..	..	..	..	..
<i>Temperature</i>							
KCl ..	62.00	..	137.4	55.78	..	6.22	..
KCl + NaCl (1) ..	55.90	14.00	133.8	42.04	14.29	13.86	..
KCl + NaCl (2) ..	55.74	26.34	124.1	29.91	26.05	25.83	..
KCl + NaCl (3) ..	54.56	37.33	116.4	21.22	35.62	33.34	1.71
KCl + NaCl (4) ..	..	..	..	..	..	..	..
NaCl ..	..	55.80	139.4	..	50.90	..	4.90
NaCl + KCl (1) ..	13.50	52.00	128.6	13.49	41.91	..	10.09
NaCl + KCl (2) ..	26.00	50.74	120.6	23.07	36.08	2.93	14.66
NaCl + KCl (3) ..	..	..	..	..	..	..	..
<i>Temperature</i>							
KCl ..	70.00	..	116.2	62.26	..	7.74	..
KCl + NaCl (1) ..	67.10	12.00	109.3	49.20	11.66	17.90	..
KCl + NaCl (2) ..	64.15	23.20	101.2	36.31	23.16	27.84	..
KCl + NaCl (3) ..	61.96	33.70	93.64	31.01	26.33	30.95	7.37
NaCl ..	..	53.00	119.4	..	46.24	..	6.76
NaCl + KCl (1) ..	14.90	50.49	111.4	14.50	37.79	..	12.70
NaCl + KCl (2) ..	27.96	48.30	103.4	28.08	30.18	..	18.12
NaCl + KCl (3) ..	41.49	46.71	107.9	35.01	30.50	6.48	16.21

## MENT I.

 $KCl, NaCl, H_2O$ .

CONCENTRATION OF SALTS IN SOLUTION.						Specific gravity  <div>weight volume</div>
Per 100 grms. water.		Per 100 moles water.		Per 100 c.c. solution.		
KCl grms.	NaCl grms.	KCl moles.	NaCl moles.	KCl grms.	NaCl grms.	
20°C.						
34.61	..	8.34	..	30.24	..	1.176
26.60	10.13	6.41	3.12	23.27	8.87	1.197
19.65	20.61	4.74	6.34	17.00	17.83	1.213
14.92	30.36	3.60	9.34	12.70	25.85	1.237
15.36	29.61	3.70	9.11	13.13	25.32	1.240
..	35.63	..	11.00	..	31.34	1.193
9.70	32.40	2.34	9.97	8.37	27.91	1.224
14.76	30.38	3.56	9.35	11.69	26.66	1.233
15.20	29.74	3.66	9.15	12.98	25.44	1.240
30°C.						
37.58	..	9.06	..	32.41	..	1.186
29.45	10.13	7.10	3.12	25.37	8.72	1.202
22.83	19.92	5.50	6.13	19.55	17.05	1.222
16.81	29.40	4.05	9.05	14.26	24.92	1.240
16.85	30.06	4.06	9.25	14.19	25.30	1.237
..	36.32	..	11.18	..	32.00	1.202
9.95	32.26	2.40	9.92	8.57	27.76	1.224
16.43	30.51	3.96	9.39	13.85	25.71	1.238
17.13	29.88	4.12	9.20	..	..	..
40°C.						
40.60	..	9.78	..	34.49	..	1.194
31.42	10.68	7.57	3.29	26.70	9.07	1.207
24.43	20.99	5.89	6.46	20.75	17.82	1.235
18.23	30.60	4.39	9.41	15.29	25.67	1.248
18.74	30.32	4.52	9.33	15.61	25.26	1.242
..	36.53	..	11.24	..	32.03	1.197
10.49	32.59	2.53	10.03	8.96	27.84	1.222
19.13	29.92	4.61	9.20	16.01	25.04	1.247
19.37	29.88	4.67	9.20	16.15	24.93	1.245
91°C.						
53.58	..	12.91	..	42.51	..	1.222
45.01	10.66	10.85	3.28	35.74	8.47	1.236
35.84	22.87	8.64	7.03	28.50	18.18	1.262
33.12	28.12	7.98	8.65	25.93	22.01	1.262
..	38.72	..	11.91	..	33.16	1.189
13.00	33.93	3.13	10.44	10.83	28.25	1.223
27.15	29.18	6.54	8.98	21.46	23.05	1.235
32.45	28.26	7.82	8.69	25.52	22.23	1.264

STATE  
The system

System.		MATERIALS IN REACTION VESSEL.							
		Initially added.			AT EQUILIBRIUM.				
					In solution.		Solid phases.		
		KCl grms.	KNO <sub>3</sub> grms.	H <sub>2</sub> O grms.	KCl grms.	KNO <sub>3</sub> grms.	KCl grms.	KNO <sub>3</sub> grms.	
								Temperature	
KCl	..	54.00	..	141.9	49.12	..	5.88	..	
KCl + KNO <sub>3</sub> (1)	..	52.00	12.00	136.1	46.00	11.90	6.00	..	
KCl + KNO <sub>3</sub> (2)	..	50.34	22.47	130.8	43.86	22.17	6.48	..	
KCl + KNO <sub>3</sub> (3)	..	48.47	31.52	124.3	41.31	26.13	7.16	8.36	
KCl + KNO <sub>3</sub> (4)	..	..	..	..	..	..	..	..	
KNO <sub>3</sub>	..	..	50.00	139.7	..	43.99	..	6.01	
KNO <sub>3</sub> + KCl (1)	..	12.90	58.17	133.6	13.16	33.04	..	25.13	
KNO <sub>3</sub> + KCl (2)	..	24.76	56.83	127.7	24.43	27.29	..	29.54	
KNO <sub>3</sub> + KCl (3)	..	34.83	55.90	122.3	34.83	23.87	..	32.03	
KNO <sub>3</sub> + KCl (4)	..	43.42	54.94	116.9	39.13	21.58	4.29	33.36	
								Temperature	
KCl	..	57.20	..	140.9	52.95	..	4.25	..	
KCl + KNO <sub>3</sub> (1)	..	56.00	11.00	141.5	51.96	11.39	4.04	..	
KCl + KNO <sub>3</sub> (2)	..	54.24	25.52	135.3	48.97	26.19	5.27	..	
KCl + KNO <sub>3</sub> (3)	..	52.21	39.34	129.1	45.66	35.11	6.55	4.23	
KCl + KNO <sub>3</sub> (4)	..	..	..	..	..	..	..	..	
KNO <sub>3</sub> + KCl (1)	..	13.00	70.10	140.2	13.23	53.42	..	16.68	
KNO <sub>3</sub> + KCl (2)	..	25.57	68.34	134.2	25.97	43.40	..	24.94	
KNO <sub>3</sub> + KCl (3)	..	36.41	66.67	127.9	36.72	37.33	..	29.34	
KNO <sub>3</sub> + KCl (4)	..	45.01	65.25	122.2	43.55	32.00	1.46	33.25	
								Temperature	
KCl	..	62.00	..	137.4	55.78	..	6.22	..	
KCl + KNO <sub>3</sub> (1)	..	53.00	20.00	118.6	46.39	20.00	6.61	..	
KCl + KNO <sub>3</sub> (2)	..	51.44	39.33	111.9	41.49	39.71	9.95	..	
KCl + KNO <sub>3</sub> (3)	..	49.61	55.58	104.8	39.34	41.73	10.27	13.85	
KCl + KNO <sub>3</sub> (4)	..	..	..	..	..	..	..	..	
KNO <sub>3</sub>	..	..	80.00	111.0	..	71.85	..	8.15	
KNO <sub>3</sub> + KCl (1)	..	11.90	77.36	104.6	12.11	55.08	..	22.28	
KNO <sub>3</sub> + KCl (2)	..	22.46	75.38	98.66	22.32	45.70	..	29.68	
KNO <sub>3</sub> + KCl (3)	..	33.41	73.43	103.7	33.22	42.81	..	30.62	
KNO <sub>3</sub> + KCl (4)	..	43.29	72.12	96.89	35.99	38.08	7.30	34.04	
								Temperature	
KCl	..	70.00	..	116.2	62.26	..	7.74	..	
KCl + KNO <sub>3</sub> (1)	..	50.00	45.00	84.70	40.54	44.70	9.46	..	
KCl + KNO <sub>3</sub> (2)	..	47.74	87.46	76.60	33.16	87.78	14.58	..	
KCl + KNO <sub>3</sub> (3)	..	45.98	122.7	71.03	28.34	115.7	17.64	6.99	
KNO <sub>3</sub>	..	..	167.3	71.30	..	144.6	..	22.70	
KNO <sub>3</sub> + KCl (1)	..	9.80	155.1	63.75	9.90	115.3	..	39.75	
KNO <sub>3</sub> + KCl (2)	..	19.09	149.1	58.95	19.60	97.65	..	51.41	
KNO <sub>3</sub> + KCl (3)	..	27.71	143.2	53.91	21.56	87.87	6.15	55.31	

## MENT II.

 $KCl$ ,  $KNO_3$ ,  $H_2O$ .

CONCENTRATION OF SALTS IN SOLUTION.						Specific gravity.  weight volume
Per 100 grms. water.		Per 100 moles water.		Per 100 c.c. solution.		
KCl grms.	KNO <sub>3</sub> grms.	KCl moles.	KNO <sub>3</sub> moles.	KCl grms.	KNO <sub>3</sub> grms.	
20°C.						
34.61	..	8.34	..	30.24	..	1.176
33.79	8.73	8.14	1.55	28.69	7.41	1.210
33.53	16.95	8.08	3.02	27.74	14.02	1.245
33.23	18.63	8.01	3.32	27.22	15.25	1.244
33.17	18.99	7.99	3.38	27.39	16.02	1.257
..	31.49	..	5.61	..	27.95	1.167
9.85	24.73	2.37	4.41	8.66	21.67	1.181
19.14	21.37	4.61	3.81	16.40	18.31	1.204
28.48	19.52	6.86	3.48	23.87	16.36	1.241
33.48	18.46	8.07	3.29	27.75	15.31	1.260
30°C.						
37.58	..	9.06	..	32.41	..	1.186
36.72	8.05	8.85	1.43	30.92	6.78	1.219
36.19	19.36	8.72	3.45	29.09	15.57	1.251
35.40	27.22	8.53	4.85	27.86	21.42	1.280
35.42	26.83	8.53	4.78	27.95	21.18	1.281
9.44	38.10	2.27	6.79	7.86	31.64	1.225
19.35	32.34	4.66	5.80	15.83	26.45	1.241
28.71	29.19	6.92	5.20	22.88	23.26	1.258
35.63	26.18	8.60	4.66	28.19	20.72	1.280
40°C.						
40.60	..	9.78	..	34.49	..	1.194
39.11	16.86	9.43	3.00	31.38	13.54	1.252
37.08	35.49	8.94	6.32	28.05	26.84	1.305
37.54	39.82	9.05	7.10	27.93	29.62	1.319
37.49	39.71	9.03	7.08	27.89	29.55	1.319
..	64.74	..	11.54	..	50.62	1.288
11.58	52.66	2.79	9.38	9.02	41.00	1.279
22.63	46.31	5.45	8.25	17.36	35.55	1.297
32.22	41.52	7.77	7.40	24.34	31.36	1.312
37.15	39.30	8.95	7.00	27.65	29.26	1.313
91°C.						
53.58	..	12.91	..	42.51	..	1.222
47.85	52.75	11.53	9.40	32.06	35.34	1.344
43.30	114.6	10.43	20.42	24.39	66.62	1.486
39.90	162.9	9.61	29.03	20.43	83.49	1.552
..	202.8	..	36.14	..	103.9	1.552
15.56	181.1	3.75	32.28	8.10	94.30	1.545
33.25	165.6	8.01	29.52	17.18	85.62	1.544
40.00	163.0	9.65	29.05	20.48	83.32	1.550

System.	MATERIALS IN REACTION VESSEL.						
	Initially added.			AT EQUILIBRIUM.			
				In solution.		Solid phases.	
	KNO <sub>3</sub> grms.	NaNO <sub>3</sub> grms.	H <sub>2</sub> O grms.	KNO <sub>3</sub> grms.	NaNO <sub>3</sub> grms.	KNO <sub>3</sub> grms.	NaNO <sub>3</sub> grms.
KNO <sub>3</sub> ..	50.00	..	139.7	43.99	..	<i>Temperature</i>	
KNO <sub>3</sub> + NaNO <sub>3</sub> (1) ..	49.90	30.30	143.0	45.46	28.90	6.01	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (2) ..	46.51	59.55	131.9	44.28	58.94	4.44	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (3) ..	49.29	84.34	119.9	44.51	83.70	2.23	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (4) ..	45.70	102.7	110.0	44.69	100.8	4.78	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (5) ..	51.35	107.4	100.7	40.31	94.90	1.01	..
NaNO <sub>3</sub> ..	..	110.0	121.1	..	106.1	11.04	12.49
NaNO <sub>3</sub> + KNO <sub>3</sub> (1) ..	9.90	111.2	116.4	9.93	103.5	..	3.90
NaNO <sub>3</sub> + KNO <sub>3</sub> (2) ..	19.05	107.6	112.0	19.00	102.2	..	7.72
NaNO <sub>3</sub> + KNO <sub>3</sub> (3) ..	27.26	103.4	107.1	27.73	98.89	..	5.42
NaNO <sub>3</sub> + KNO <sub>3</sub> (4) ..	34.33	100.1	103.2	34.25	96.82	..	5.48
NaNO <sub>3</sub> + KNO <sub>3</sub> (5) ..	46.10	106.6	98.00	38.94	92.40	..	3.25
						7.16	14.20
KNO <sub>3</sub> + NaNO <sub>3</sub> (1) ..	67.00	30.00	112.3	51.35	29.09	<i>Temperature</i>	
KNO <sub>3</sub> + NaNO <sub>3</sub> (2) ..	64.87	56.79	106.8	50.48	56.12	15.65	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (3) ..	63.11	81.85	102.4	52.21	81.28	14.39	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (4) ..	60.98	105.6	97.57	53.02	100.8	10.90	..
NaNO <sub>3</sub> ..	..	118.0	118.6	..	113.7	7.96	4.75
NaNO <sub>3</sub> + KNO <sub>3</sub> (1) ..	15.00	115.0	105.6	15.10	104.6	..	4.30
NaNO <sub>3</sub> + KNO <sub>3</sub> (2) ..	30.46	111.3	101.1	30.56	102.5	..	10.40
NaNO <sub>3</sub> + KNO <sub>3</sub> (3) ..	45.69	108.7	97.81	46.63	100.8	..	8.79
NaNO <sub>3</sub> + KNO <sub>3</sub> (4) ..	60.17	105.4	93.92	51.56	97.70	..	7.90
						8.61	7.71
KNO <sub>3</sub> ..	80.00	..	111.0	71.85	..	<i>Temperature</i>	
KNO <sub>3</sub> + NaNO <sub>3</sub> (1) ..	79.70	26.20	109.8	69.40	26.19	8.15	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (2) ..	77.57	52.28	104.2	66.52	51.86	10.30	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (3) ..	75.15	77.39	97.2	64.55	77.20	11.05	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (4) ..	72.58	104.3	91.00	65.20	102.0	10.60	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (5) ..	77.31	107.9	85.67	63.45	99.55	7.38	..
NaNO <sub>3</sub> ..	..	114.7	100.9	..	106.1	13.86	8.37
NaNO <sub>3</sub> + KNO <sub>3</sub> (1) ..	22.00	120.0	106.6	21.67	117.2	..	8.60
NaNO <sub>3</sub> + KNO <sub>3</sub> (2) ..	42.81	125.1	98.32	43.18	110.3	..	2.80
NaNO <sub>3</sub> + KNO <sub>3</sub> (3) ..	63.15	120.8	92.23	63.38	107.1	..	14.77
NaNO <sub>3</sub> + KNO <sub>3</sub> (4) ..	82.55	117.3	86.98	63.42	100.5	..	13.70
						19.13	16.80
KNO <sub>3</sub> ..	167.3	..	71.30	144.6	..	<i>Temperature</i>	
KNO <sub>3</sub> + NaNO <sub>3</sub> (1) ..	144.7	25.00	58.30	117.1	25.30	22.70	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (2) ..	137.6	48.27	52.28	108.3	48.60	27.60	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (3) ..	131.7	70.60	45.41	104.2	70.93	29.35	..
KNO <sub>3</sub> + NaNO <sub>3</sub> (4) ..	128.1	90.84	40.93	102.1	84.15	27.49	..
NaNO <sub>3</sub> ..	..	139.9	76.00	..	122.2	26.03	6.69
NaNO <sub>3</sub> + KNO <sub>3</sub> (1) ..	39.80	133.5	70.50	39.30	122.0	..	17.70
NaNO <sub>3</sub> + KNO <sub>3</sub> (2) ..	82.23	131.9	64.29	82.61	119.6	..	11.50
NaNO <sub>3</sub> + KNO <sub>3</sub> (3) ..	109.5	118.5	51.47	109.0	102.9	..	12.28
NaNO <sub>3</sub> + KNO <sub>3</sub> (4) ..	135.2	112.1	43.33	109.1	89.48	..	15.58
						26.14	22.65



## MENT III.

 $KNO_3$ ,  $NaNO_3$ ,  $H_2O$ .

CONCENTRATION OF SALTS IN SOLUTION.						Specific gravity.
Per 100 grms. water.		Per 100 moles water.		Per 100 c.c. solution.		
KNO grms.	NaNO <sub>3</sub> grms.	KNO <sub>3</sub> Moles.	NaNO <sub>3</sub> Moles.	KNO <sub>3</sub> grms.	NaNO <sub>3</sub> grms.	
						<div>weight</div> <div>volume</div>
20°C.						
31.49	..	5.61	..	27.95	..	1.167
31.79	20.19	5.67	4.27	26.38	16.75	1.261
33.53	44.65	5.98	9.44	25.35	33.74	1.347
37.10	69.75	6.61	14.75	25.66	48.25	1.431
40.63	91.67	7.24	19.40	26.16	59.01	1.495
40.03	94.27	7.13	19.94	25.60	60.29	1.499
..	87.60	..	18.53	..	64.64	1.384
8.54	88.92	1.52	18.81	6.10	63.57	1.412
16.96	91.20	3.02	19.30	11.76	63.21	1.443
25.92	92.42	4.62	19.55	17.34	61.83	1.461
33.18	93.82	5.91	19.84	21.66	61.21	1.481
39.73	94.27	7.08	19.94	25.36	60.19	1.494
30°C.						
45.73	25.90	8.15	5.50	35.09	19.87	1.317
47.25	52.53	8.42	11.10	33.18	36.89	1.403
50.93	79.27	9.08	16.80	32.57	50.69	1.472
54.34	103.3	9.70	21.85	32.58	61.89	1.544
..	95.90	..	20.30	..	68.85	1.406
14.30	99.10	2.55	21.00	9.72	58.24	1.451
30.25	101.6	5.40	21.46	19.33	64.89	1.481
47.67	103.1	8.50	21.80	28.89	62.48	1.520
54.90	104.0	9.80	22.00	32.47	61.53	1.532
40°C.						
64.74	..	11.54	..	50.62	..	1.288
63.21	23.85	11.27	4.84	45.02	17.49	1.358
63.86	49.79	11.38	10.53	42.68	33.27	1.428
66.44	79.46	11.84	16.80	40.65	48.63	1.505
71.64	112.0	12.77	23.68	39.75	62.11	1.573
74.06	116.2	13.20	24.58	40.04	62.88	1.570
..	105.2	..	22.25	..	72.87	1.421
20.33	109.9	3.62	23.24	13.03	70.44	1.476
43.92	112.2	7.83	23.73	26.16	66.85	1.526
68.72	116.2	12.25	24.56	37.95	64.14	1.573
72.89	115.5	12.99	24.43	39.95	63.35	1.581
91°C.						
202.8	..	36.14	..	103.9	..	1.552
200.8	43.40	35.80	9.18	94.44	20.17	1.615
207.2	92.90	36.93	19.65	86.71	38.87	1.674
229.5	156.2	40.90	33.03	82.72	56.28	1.751.
249.4	205.6	44.45	43.50	80.41	66.31	1.790
..	160.8	..	34.00	..	93.76	1.521
55.75	173.1	9.90	36.61	27.30	84.75	1.610
128.5	186.0	22.90	39.34	52.54	76.06	1.695
211.7	200.0	37.73	42.30	73.39	69.33	1.774
251.8	206.5	44.86	43.67	80.46	66.04	1.785

STATE  
*The System*

System.	MATERIALS IN REACTION VESSEL.						
	Initially added.			AT EQUILIBRIUM.			
				In solution.		Solid phases.	
	NaNO <sub>3</sub> grms.	NaCl grms.	H <sub>2</sub> O grms.	NaNO <sub>3</sub> grms.	NaCl grms.	NaNO <sub>3</sub> grms.	NaCl grms.
						<i>Temperature</i>	
NaNO <sub>3</sub> .. ..	110.0	..	121.1	106.1	..	3.90	..
NaNO <sub>3</sub> + NaCl (1) ..	107.4	12.00	117.5	84.60	12.06	22.80	..
NaNO <sub>3</sub> + NaCl (2) ..	103.6	23.39	112.1	65.53	23.42	38.03	..
NaNO <sub>3</sub> + NaCl (3) ..	101.1	33.58	107.4	58.46	26.74	42.58	6.84
NaNO <sub>3</sub> + NaCl (4) ..	..	..	..	..	..	..	..
NaCl .. ..	..	56.00	138.7	..	49.41	..	6.59
NaCl + NaNO <sub>3</sub> (1) ..	29.90	53.00	124.4	29.87	38.50	..	14.50
NaCl + NaNO <sub>3</sub> (2) ..	58.86	51.40	118.9	58.57	30.62	..	20.78
NaCl + NaNO <sub>3</sub> (3) ..	81.52	50.18	113.2	61.08	28.26	20.44	21.92
NaCl + NaNO <sub>3</sub> (4) ..	..	..	..	..	..	..	..
						<i>Temperature</i>	
NaNO <sub>3</sub> .. ..	118.0	..	118.6	113.7	..	4.30	..
NaNO <sub>3</sub> + NaCl (1) ..	113.6	11.00	113.2	92.21	11.04	21.43	..
NaNO <sub>3</sub> + NaCl (2) ..	109.4	20.99	107.1	72.73	21.09	36.70	..
NaNO <sub>3</sub> + NaCl (3) ..	106.4	30.11	101.8	64.54	23.82	41.85	6.29
NaCl .. ..	..	53.00	128.4	..	46.64	..	6.36
NaCl + NaNO <sub>3</sub> (1) ..	29.90	51.14	122.4	29.63	38.15	..	12.99
NaCl + NaNO <sub>3</sub> (2) ..	56.57	49.57	116.1	55.90	30.59	..	18.98
NaCl + NaNO <sub>3</sub> (3) ..	79.83	48.62	111.4	70.27	26.18	..	22.44
NaCl + NaNO <sub>3</sub> (4) ..	..	..	..	..	..	..	..
						<i>Temperature</i>	
NaNO <sub>3</sub> .. ..	114.7	..	100.9	106.1	..	8.6	..
NaNO <sub>3</sub> + NaCl (1) ..	125.0	12.00	112.8	101.4	12.18	23.59	..
NaNO <sub>3</sub> + NaCl (2) ..	121.4	23.57	106.5	80.26	23.04	41.15	0.53
NaNO <sub>3</sub> + NaCl (3) ..	118.2	33.75	100.1	74.02	21.72	44.21	12.03
NaCl .. ..	..	55.80	139.4	..	50.90	..	4.90
NaCl + NaNO <sub>3</sub> (1) ..	35.00	52.89	126.0	34.41	38.47	..	14.42
NaCl + NaNO <sub>3</sub> (2) ..	63.35	51.25	117.7	64.52	31.19	..	20.06
NaCl + NaNO <sub>3</sub> (3) ..	90.93	50.08	110.8	81.95	24.24	8.98	25.84
NaCl + NaNO <sub>3</sub> (4) ..	..	..	..	..	..	..	..
						<i>Temperature</i>	
NaNO <sub>3</sub> .. ..	139.9	..	76.00	122.2	..	17.70	..
NaNO <sub>3</sub> + NaCl (1) ..	130.0	7.00	80.00	119.6	7.22	10.40	..
NaNO <sub>3</sub> + NaCl (2) ..	122.9	13.47	66.94	94.60	10.60	28.29	2.87
NaNO <sub>3</sub> + NaCl (3) ..	..	..	..	..	..	..	..
NaCl .. ..	..	53.00	119.4	..	46.24	..	6.76
NaCl + NaNO <sub>3</sub> (1) ..	40.00	41.90	106.7	39.94	32.23	..	9.67
NaCl + NaNO <sub>3</sub> (2) ..	77.32	39.74	97.04	77.29	22.48	..	17.26
NaCl + NaNO <sub>3</sub> (3) ..	112.0	38.24	88.38	112.4	15.07	..	23.17
NaCl + NaNO <sub>3</sub> (4) ..	134.9	36.64	77.46	110.0	12.31	24.90	24.33

## MENT IV.

 $\text{NaNO}_3$ ,  $\text{NaCl}$ ,  $\text{H}_2\text{O}$ .

CONCENTRATION OF SALTS IN SOLUTION.						Specific gravity.
Per 100 grms. water.		Per 100 moles water.		Per 100 c.c. solution.		
NaNO <sub>3</sub> grms.	NaCl grms.	NaNO <sub>3</sub> moles.	NaCl moles.	NaNO <sub>3</sub> grms.	NaCl grms.	<u>weight</u> <u>volume</u>
20°C.						
87.60	..	18.53	..	64.64	..	1.384
71.99	10.27	15.23	3.16	54.44	7.76	1.378
58.46	20.89	12.36	6.43	44.35	15.85	1.361
54.34	24.89	11.50	7.66	41.52	19.02	1.370
53.79	24.98	11.40	7.69	41.03	19.06	1.364
..	35.63	..	11.00	..	31.34	1.193
24.01	30.93	5.08	9.52	20.02	25.81	1.293
49.24	25.75	10.41	7.92	38.14	19.94	1.356
53.96	24.97	11.41	7.68	41.13	19.03	1.364
53.64	24.72	11.34	7.59	41.00	18.84	1.362
30°C.						
95.90	..	20.30	..	68.85	..	1.406
81.46	9.76	17.23	3.00	59.38	7.11	1.394
67.91	19.69	14.36	6.06	50.00	14.50	1.381
63.40	23.40	13.41	7.20	47.11	17.38	1.388
..	36.30	..	11.18	..	32.00	1.202
24.21	31.16	5.12	9.59	19.88	25.60	1.276
48.15	26.35	10.18	8.11	37.04	20.27	1.343
63.08	23.50	13.34	7.23	46.63	17.38	1.379
62.96	23.54	13.31	7.24	46.51	17.40	1.378
40°C.						
105.2	..	22.25	..	72.87	..	1.421
89.90	10.80	19.01	3.33	63.14	7.61	1.410
75.29	21.61	15.92	6.65	53.39	15.32	1.396
74.01	21.71	15.65	6.68	52.83	15.49	1.397
..	36.53	..	11.24	..	32.03	1.197
27.31	30.53	5.78	9.39	22.23	24.84	1.284
54.82	26.50	11.60	8.15	40.02	19.34	1.323
73.96	21.87	15.64	6.73	53.23	15.74	1.409
73.72	21.68	15.59	6.67	52.69	15.49	1.397
91°C.						
160.8	..	34.00	..	93.76	..	1.521
149.5	9.03	31.62	2.78	86.96	5.25	1.504
141.3	15.83	29.90	4.87	83.42	9.34	1.518
140.9	15.97	29.81	4.91	83.96	9.52	1.531
..	38.72	..	11.91	..	33.16	1.189
37.43	30.21	7.92	9.29	28.93	23.35	1.296
79.65	23.17	16.85	7.13	54.23	15.78	1.381
127.2	17.05	26.90	5.25	77.65	10.14	1.487
142.0	15.89	30.02	4.89	83.07	9.30	1.509

The first consideration is a comparison between the concentrations found in any system, on the one hand when salt B was added to the saturated solution of A until B appeared also as a solid phase, on the other hand when salt A was added to the saturated solution of B until A was in excess. This comparison of the data in the statements shows that the agreement between the concentrations when both salts were in excess was very close indeed, the differences being quite small, and hence the concentrations found are reliable. Then the chart as well as the data shows for the first four systems readily what the effect is of adding one salt to the solution of the other. It is perfectly regular at all temperatures and is simple ;

(a) in the case of systems—

(vii) NaCl, KCl,  $H_2O$ .

(viii) KCl,  $KNO_3$ ,  $H_2O$ .

(vi)  $NaNO_3$ , NaCl,  $H_2O$ .

the one salt *decreases* the solubility of the other salt.

(b) In the case of system—

(v)  $KNO_3$ ,  $NaNO_3$ ,  $H_2O$ .

the one salt *increases* the solubility of the other salt.

The case of the ninth system,  $KNO_3 + NaCl$ , will be separately considered.

Further the chart shows very definitely that this effect of the one salt on the solubility of the other is not a simple linear one, but that it is logarithmic ; the curves on the chart are simply hand drawn through the points representing the determinations, as it was not considered worth while to calculate the values for the thirty-two curves which are derivable from the data.

In one case, namely, the curves representing the solubility of  $NaNO_3$  in NaCl saturated solution at  $30^\circ$  and  $40^\circ$  C. the two lie so close together that they could not be separated on the scale of the original chart, which was about four times that of the reproduction, and this explains the presence of only three curves in this section.

As regards the *relative* effect of one salt on the solubility of the other in these four systems, the ratios which are set out in the following statement are interesting:—

*Effects of added salts.*

	20°C.		30°C.		40°C.		91°C.	
	Relative Increase.	Relative Decrease.	Relative Increase.	Relative Decrease.	Relative Increase.	Relative Decrease.	Relative Increase.	Relative Decrease.
KCl on NaCl ..	..	·835	..	·823	..	·818	..	·733
NaCl on KCl ..	..	·444	..	·448	..	·462	..	·618
KNO <sub>3</sub> on KCl ..	..	·958	..	·943	..	·923	..	·745
KCl on KNO <sub>3</sub> ..	..	·586	..	·588	..	·607	..	·804
NaNO <sub>3</sub> on KNO <sub>3</sub>	1·271	..	1·221	..	1·143	..	1·225	..
KNO <sub>3</sub> on NaNO <sub>3</sub>	1·076	..	1·085	..	1·098	..	1·280	..
NaCl on NaNO <sub>3</sub>	..	·614	..	·661	..	·703	..	·876
NaNO <sub>3</sub> on NaCl	..	·694	..	·648	..	·593	..	·411

These ratios are simply the relative solubility of a salt A when the second salt B is present in excess ; the solubility of A when alone being taken as unity. They show clearly how the presence of one nitrate *increases* the solubility of the other nitrate, whereas in all other cases the solubility is decreased when a second salt is added. The ratios vary with the temperature systematically, either increasing or decreasing.

*The system KNO<sub>3</sub>, NaCl, H<sub>2</sub>O.*

The data relating to the ninth system is left for separate consideration because it is naturally more complicated. It is a system of four components (including water) and there will be therefore, when excess of both the initial salts is present and at a fixed temperature, five phases, three of which are solid ; over a certain interval however there may be present only one or two solid phases. There may also be a transition point.

It has already been remarked how that, considering the commercial importance of the relations of these salts, the published information is remarkably limited. Löwenherz<sup>1</sup> has published

<sup>1</sup>*Zeits. f. Phys. Chemie.* XIII, 459.

a theoretical consideration of the system, but gives no details of the concentrations that he obtained at the temperature he employed which was  $25^{\circ}\text{C}$ . He makes the remarkable statement that  $\text{KNO}_3$  and  $\text{NaCl}$  cannot exist together in solution. So far as this point is concerned, it is only necessary to bear in mind the fact that if sodium nitrate is added to concentrated potassium chloride solution, sodium chloride is precipitated, in order to realise that the statement is not correct. Etard<sup>1</sup> has published data of the solubility of a mixture of  $\text{KNO}_3$  and  $\text{NaCl}$  in water at temperatures between  $0^{\circ}$  and  $170^{\circ}$ . These data, grms. per 100 grms. solution, compare, after translation into the terms adopted by us, fairly well with ours, *but he leaves the third salt, which must be present in the saturated solution, unnoticed.*

E. Janecke<sup>2</sup> quotes data which were obtained by Kenjiro Uyeda-Kyoto at  $25^{\circ}\text{C}$ . which also agree with ours, but he enters the same three salts, namely,  $\text{NaCl}$ ,  $\text{NaNO}_3$  and  $\text{KNO}_3$  as being in solution and as the solid phases together.

An examination of statement V shows that *up to certain concentrations (i)* at temperatures  $20^{\circ}$  and  $30^{\circ}\text{C}$ . the solubility of the one salt is increased by the addition of the other; at  $40^{\circ}\text{C}$ . this also applies to the effect of  $\text{KNO}_3$  on the solubility of  $\text{NaCl}$ , but that the solution of  $\text{KNO}_3$  remains approximately constant for successive additions of  $\text{NaCl}$ ; at  $90^{\circ}$  the solubility of each salt is increased by the other.

(ii) The character of the system at low concentrations of one salt is simple, for up to a certain point the solid phase consists simply of that which is initially present in excess.

(iii) After the quantity of the second salt, say B, exceeds a certain limit, a new solid phase, say C, commences to form, whilst at the same time an equivalent quantity of D is formed in the solution.

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<sup>1</sup> *Ann. Chem. Phys.* (7) 3, 383.

<sup>2</sup> *Zeits. f. anorg. chem.*, 1911, LXXI, p. 1.



Continued addition of salt B causes a continued formation of salts C and D until the concentration of D in the solution reaches a certain limit. Among our experiments at temperature  $91^{\circ}\text{C}$  there are several interesting instances. Following the upper section statement V in which NaCl was added gradually to a solution of  $\text{KNO}_3$  containing  $\text{KNO}_3$  in excess, this salt was present as solid phase until more than 22.95 grms. NaCl had been added. Further addition of NaCl to 31.02 grms. caused a precipitation of KCl accompanied naturally by the formation of an equivalent amount of  $\text{NaNO}_3$  in solution, which change was made at the expense of the solid  $\text{KNO}_3$ , so that this disappeared and the only solid phase for the time being was KCl. Further addition of  $\text{KNO}_3$  and NaCl caused complete saturation and both these salts appeared as solid phases. Similarly when  $\text{KNO}_3$  was added in portions to a saturated solution of NaCl including NaCl as solid phase, a point was reached when KCl was precipitated, and an equivalent quantity of  $\text{NaNO}_3$  formed in the solution, the change being effected at the expense of the NaCl which was present as solid phase; at this stage there was again only KCl as solid phase, whilst the solution contained the three salts,  $\text{KNO}_3$ , NaCl,  $\text{NaNO}_3$ . Further addition of  $\text{KNO}_3$  caused first an increase of both KCl and  $\text{NaNO}_3$  until when the  $\text{NaNO}_3 = 6.94$  moles per 100 moles water, the formation of  $\text{NaNO}_3$  and KCl ceased, and  $\text{KNO}_3$  appeared as a solid phase; thus there were at this stage two solid phases.

The case is best exemplified by data taken from statement V for temperature  $91^{\circ}\text{C}$  and which are:—

*Quantities expressed in moles per 100 moles water.*

No.	Total salts used.		Salts present in solution.			Solids.
	$\text{KNO}_3$	NaCl	$\text{KNO}_3$	NaCl	$\text{NaNO}_3$	
1	22.8	15.3	22.62	13.64	...	NaCl
2	35.5	18.2	31.33	12.57	4.65	KCl
3	50.5	19.2	38.24	11.97	6.94	KCl, $\text{KNO}_3$
4	42.0	11.1	37.55	11.00	...	$\text{KNO}_3$
5	43.1	16.3	38.01	11.67	5.18	KCl
6	53.8	23.8	38.99	12.03	6.88	KCl, $\text{KNO}_3$ , NaCl

In this the quantities of salts and water employed as also those present in solution and as solid phases are expressed as moles per 100 moles water.

Thus :—

- (i) On adding NaCl to a saturated solution of  $\text{KNO}_3$  in presence of excess  $\text{KNO}_3$ , the solid phase is  $\text{KNO}_3$ , until more than about 11.25 moles NaCl have been added. Further addition of NaCl then causes the change  $\text{KNO}_3 + \text{NaCl} = \text{NaNO}_3 + \text{KCl}$  to set in with precipitation of KCl. This change continues until the concentration of  $\text{NaNO}_3$  in the solution reaches 6.9 moles, when further addition of NaCl simply remains undissolved. It is assumed that for the above changes there is sufficient  $\text{KNO}_3$  in the solid state to provide for the complete change, *i.e.*, at least 6.9 moles. Excess of  $\text{KNO}_3$  above this quantity remains as a solid phase.
- (ii) On adding  $\text{KNO}_3$  to the saturated solution of NaCl and in presence of an excess of this salt, the precipitation of KCl commences when the concentration of  $\text{KNO}_3$  exceeds about 26.6 moles and continues (assuming of course a sufficient excess of NaCl) until the concentration of  $\text{NaNO}_3$  reaches 6.9 moles, after which further additions of  $\text{KNO}_3$  remain undissolved.

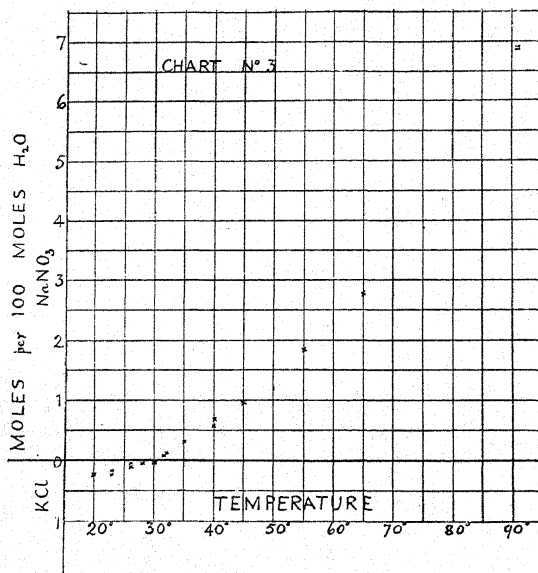
This example is the best we have, because at this temperature the quantities of  $\text{NaNO}_3$  and KCl which appear subsequent to certain concentrations are much in excess of an experimental error.

The concentration of the solution which is obtained when excess of  $\text{NaNO}_3$  and KCl are employed has been ascertained at  $t = 40^\circ\text{C}$ . The data thus obtained are set out below in conjunction with those which were obtained from  $\text{KNO}_3$  *plus* NaCl.

				grms. per 100 grms. H <sub>2</sub> O		
				KNO <sub>3</sub>	NaCl	NaNO <sub>3</sub>
1	ex	NaNO <sub>3</sub> + KCl	.. ..	.. 64.25	38.73	3.04
2.	ex	KNO <sub>3</sub> + NaCl	.. ..	.. 64.77	38.79	2.87
3.	ex	NaCl + KNO <sub>3</sub>	.. ..	.. 64.66	39.06	3.28

*Transition point.*

With an excess of KNO<sub>3</sub> and NaCl at temperatures down to 31° C., measurable amounts of KCl are formed as solid phase together with equivalent quantities of NaNO<sub>3</sub> in solution. At temperature 28° and lower on the other hand, in presence of excess of KNO<sub>3</sub> and NaCl, a measurable amount of NaNO<sub>3</sub> is found in the solid phase, with an equivalent of KCl in solution. There is thus a transition in the nature of the solution and solid phase respectively. Statement No. VI shows the quantities of salts found



in solutions at different temperatures between 20° and 91° C. On chart No. 3 the concentrations *in moles per 100 moles water* of KCl and NaNO<sub>3</sub> respectively, at increasing temperatures, are set out.

Statement VI—Excess of  $\text{KNO}_3$  + excess of  $\text{NaCl}$  between temperatures  $20^\circ\text{C}$ . and  $91^\circ\text{C}$ .

Temperature.	Parts per 100 parts $\text{H}_2\text{O}$ .				Moles per 100 moles $\text{H}_2\text{O}$ .	
	$\text{KNO}_3$	$\text{NaCl}$	$\text{KCl}$	$\text{NaNO}_3$	$\text{KCl}$	$\text{NaNO}_3$
$20^\circ\text{C}$	37.12	37.77	1.01	..	.24	..
$22.9^\circ\text{C}$	41.05	38.55	.67	..	.16	..
$23^\circ\text{C}$	41.15	38.00	.95	..	.23	..
$23^\circ\text{C}$	41.00	37.86	1.16	..	.28	..
$25.9^\circ\text{C}$	45.16	38.96	.30	..	.072	..
$26^\circ\text{C}$	44.87	38.75	.40	..	.10	..
$26^\circ\text{C}$	44.84	38.93	.30	..	.07	..
$26^\circ\text{C}$	44.98	38.98	.21	..	.051	..
$28^\circ\text{C}$	47.35	38.96	.17	..	.041	..
$28^\circ\text{C}$	47.38	39.16	.11	..	.027	..
$29.8^\circ\text{C}$	49.42	39.11	.17	..	.041	..
$29.9^\circ\text{C}$	50.07	39.08	<i>Nil.</i>	..	<i>Nil.</i>	..
$30^\circ\text{C}$	49.24	38.72	..	..	..	..
$30^\circ\text{C}$	49.26	39.08	..	..	..	..
$31.7^\circ\text{C}$	52.68	39.05	..	.40	..	.09
$32^\circ\text{C}$	52.49	38.84	..	.63	..	.13
$32.2^\circ\text{C}$	52.60	39.13	..	.56	..	.12
$34.8^\circ\text{C}$	56.32	39.14	..	1.30	..	.28
$34.9^\circ\text{C}$	56.76	39.27	..	1.49	..	.32
$35^\circ\text{C}$	57.18	38.75	..	1.54	..	.32
$40^\circ\text{C}$	64.66	39.06	..	3.28	..	.69
$40^\circ\text{C}$	64.02	39.18	..	2.33	..	.49
$40^\circ\text{C}$	63.92	39.23	..	3.00	..	.63
$45^\circ\text{C}$	73.35	38.92	..	4.42	..	.94
$55^\circ\text{C}$	94.00	38.74	..	8.71	..	1.84
$65^\circ\text{C}$	119.50	38.47	..	13.07	..	2.76
$91^\circ\text{C}$	218.80	39.08	..	32.52	..	6.88

## INTRODUCTORY

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IN 1909 we published<sup>1</sup> data respecting the system water, calcium carbonate, carbonic acid, at temperatures varying from 20° to 40° C. and for a partial pressure of CO<sub>2</sub> in the gas phase which varied from zero to about 35%.

In the first part of the present Memoir we provide similar data for the corresponding system magnesium carbonate, carbonic acid and water.

The second part deals with the more complex system, calcium carbonate, magnesium carbonate, carbonic acid, water.

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<sup>1</sup> *Mem. Dept. Agri. Ind., Chem. Ser., Vol. I, No. 7.*





## THE SYSTEMS :—

(A) WATER, MAGNESIUM CARBONATE AND  
CARBONIC ACID,

(B) WATER, CALCIUM CARBONATE, MAGNESIUM  
CARBONATE AND CARBONIC ACID.

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### PART I.

*The system  $\text{MgCO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  in contact with air.*

THE investigation of the system  $\text{MgCO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , air, is obviously similar to that of the corresponding  $\text{CaCO}_3$  system, but differs from it chiefly by the fact that the magnesium bicarbonate solution is very much more stable and hence requires a much longer period of time to come into equilibrium with the gas phase. It is also very much more soluble in water.

*Preparation of pure  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ .*—Pure magnesium chloride in solution was precipitated by the addition of sodium carbonate, and the magnesium carbonate was washed with  $\text{CO}_2$ -free distilled water, until free from sodium, as determined by the flame test. Another method which was adopted during the earlier stages of the work, consisted in dissolving magnesium carbonate or magnesium oxide in water by carbonic acid and agitating the clear solu-

tion of the bicarbonate with air. The precipitated carbonate was again dissolved and precipitated twice. Analysis showed that it consisted of  $\text{MgCO}_3, 3\text{H}_2\text{O}$ .

*Preparation of solution of  $\text{Mg}(\text{HCO}_3)_2$ .*—Magnesium carbonate was agitated with water and carbon dioxide gas in stoppered bottles, the air being first displaced, at room temperature, until the absorption of carbon dioxide ceased. The undissolved carbonate was allowed to settle and the clear solution was drawn off as required.

*Method of obtaining equilibrium.*—As a consequence of the comparative stability of the bicarbonate, the agitating machine which had been employed in the case of calcium bicarbonate was found to be unsuited to our present purpose. Indeed it was some time before a suitable machine was devised and constructed. For, in order to obtain equilibrium in this system it is necessary to maintain the mixture in a state of rapid agitation for at least a number of days, and at the same time to provide that the total pressure in the apparatus shall be very frequently corrected to that of the atmosphere. For some time bottles containing the solutions, plus gas were rotated on a frame in a large tank of water, but the agitation proved to be too moderate. Finally the apparatus which is illustrated in Figs. I and II was constructed and was found to answer the requirements of the case. Fig. I is a sectional elevation. A is a tank measuring 3 feet by 3 feet by 3 feet filled with water. Its temperature is maintained constant, when above the room temperature by means of a lamp underneath and a Novy's thermo-regulator; when a temperature lower than that of the atmosphere was required, ice was added periodically. A stirrer maintained the water in circulation. The body of water was so large that the temperature of this tank was readily maintained within  $5^\circ\text{C}$ . of that desired. In the centre of the tank A was a smaller tank, D, measuring  $24'' \times 16'' \times 14''$ , the upper edge of which was 6'' below that of the large water tank; it was fixed rigidly to the large tank by bolted rods. Inside tank D, a wooden box H, fitted to contain six reaction bottles, was suspended by chains C. C.

FIG. I AGITATOR

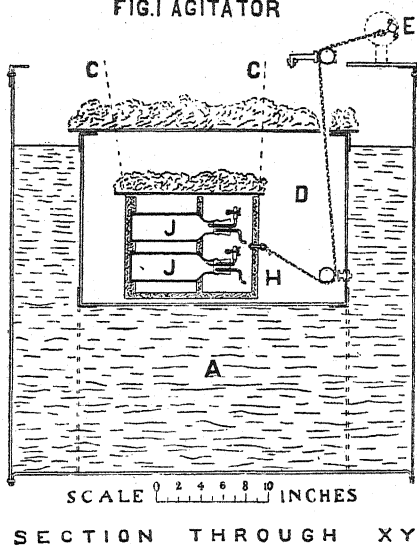


FIG. II- AGITATOR

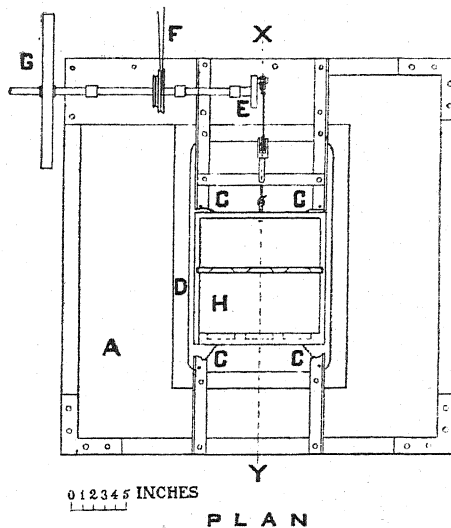
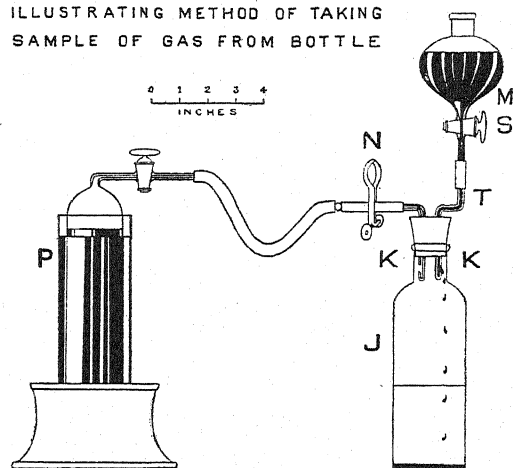


FIG. III

ILLUSTRATING METHOD OF TAKING  
SAMPLE OF GAS FROM BOTTLE





(Fig. II) at either end. At the front it was connected by a cord through pulleys to the crank-disc E, and motion to the latter was provided by the belt F from a hot-air engine. G is a fly-wheel to provide for momentum. During one-half of a revolution of the disc E, the cord was tight and drew the box H forward; during the second-half revolution the cord became slack and the box H swung back. The motion given to box H was thus an irregular one, and caused the liquid in the bottles to splash. The agitation was thus as good as though each bottle was shaken by hand. The bottles are illustrated at J in Fig. I and more perfectly in Fig. III. Each was closed by a rubber stopper through which two pieces of manometer tube were passed. These tubes were bent as shown in the figure and that mouth of each tube, which was towards the inside of the bottle, was blown *at the side* of the tube (K. Fig. III). Thus by drawing either tube into the rubber stopper, its mouth became automatically closed. If a tube was pushed into the bottle its mouth communicated with the atmosphere. During the agitation of the bottles in box H, one of the two tubes was drawn into the stopper and remained closed; the other was pushed into the bottle, but was fitted with an india-rubber tube and pinch-cock at the outer end. Hence in order to bring the pressure of the gas inside the bottle into equilibrium with the atmosphere, it was only necessary to open the pinch-cock. It was necessary however to provide that the liquid in the bottle did not cover the end of this tube; the pressure in the bottle was usually initially above that of the atmosphere, and had the bottle contained too much liquid a portion of this would naturally have been ejected when the pinch-cock was compressed. For the first short time after mixing the liquids in the bottles, as detailed below, the bottles were hand-shaken repeatedly so as to allow of the more ready escape of the first and larger portion of the gas.

It will have been noticed that whilst the tank D was immersed in the water of tank A up to near its upper edge, its upper face had to be protected and insulated. In order to provide for this, a thick quilt of cottonwool was placed on the bottles of box H, and

the tank D had a loose wooden cover over which another cotton-wool quilt was spread. Whilst therefore the temperature of the box H could not be expected to coincide exactly with that of the water in tank A, it became very uniform and constant and the temperature of tank A was accordingly regulated so that the temperature in box H became what was desired.

*Ascertaining the temperature in box H.*—It would not have been sufficiently accurate to place a thermometer in box H and to take it out in order to observe it, for its temperature would have often suffered change in doing so. In order to ascertain this temperature correctly, a small thermometer, graduated to  $0.2^{\circ}\text{C}$ . was passed through a rubber stopper which fitted a tube of water. This tube of water remained in box H, and, provided it had remained there for a sufficient time to assume the temperature of H, it could be taken out and the thermometer read without the latter suffering any appreciable change of temperature.

We have described this apparatus in detail because we have met with no similar one in the literature.

*Method of obtaining suitable mixtures.*—The preliminary work on this system although not accurate, had provided approximate information as to the quantity of magnesium carbonate which remains in solution under specified conditions of temperature and  $\text{CO}_2$  partial pressure. It was comparatively easy then to place in any bottle that quantity of concentrated magnesium bicarbonate solution and water which would eventually yield a partial pressure of approximately  $x\%$   $\text{CO}_2$ . A quantity of precipitated magnesium carbonate was also added. As will be seen from the data on pp. 213-217, the partial pressures at equilibrium were well distributed between the desired limits.

After introducing the measured portion of concentrated bicarbonate solution and the required amount of water together with some precipitated  $\text{MgCO}_3$ , the stopper was inserted and the mixture hand-shaken, whereby carbon dioxide was evolved; the clip was therefore opened repeatedly during the period of hand-shaking,

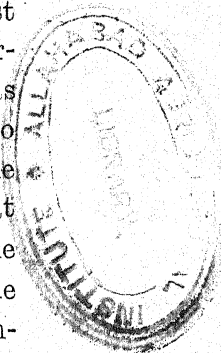


and the latter continued until the evolution of  $\text{CO}_2$  gas became negligibly small during short periods of time. The bottle was then placed in the shaking machine. The evolution of  $\text{CO}_2$  continued of course for days, but the amount subsequently evolved could be readily released by periodical opening of the pinch-cocks. It was natural that some drops of liquid were always present in the capillary tube N and the movement of these drops served as the indicator of difference of pressure between the gas in the bottle and the atmosphere.

*Method of obtaining samples of the liquid and gas phases.*—When by repeatedly opening the pinch-cocks of the bottles in the shaking machine it was ascertained that the internal pressure had ceased to change, it was assumed that equilibrium between the three phases had set in. It was naturally necessary, in order to be sure of this, that the temperature had remained constant and also that a sufficient time elapsed between tests. Usually the agitation was continued for at least a full 24 hours after no further alteration of pressure inside the bottle was observed.

It was then necessary to determine the composition of both the liquid and the gas phases. For this purpose the bottle must be removed from the shaking machine without any greater alteration of temperature than could be avoided, and samples of the gas and liquid must be removed without change of composition. To this end the following mode of operating was adopted:—The bottle was removed from the shaking machine and immersed at the tank in a large glass vessel containing water at the same temperature as that of the shaking machine; thus each bottle was subjected to a minimum of exposure to the room temperature.

A sample of the gas was then withdrawn as follows:—(See Fig. III). The exit tube of the Plimpton gas-holder P was filled with mercury and was then connected with the rubber tube of capillary N; the other capillary tube T of the reaction bottle was con-



nected to the mercury reservoir M, the outlet tube of which had been already filled with mercury ; the lower end of this capillary T was then pushed into the bottle. On opening the clip N communication was made between the gas in the bottle, and the Plimpton gas-holder, whilst on opening the tap S communication was made between the mercury reservoir and the reaction bottle. Both clip and tap were opened as simultaneously as possible and the flow of mercury was regulated so that the gas could flow into the gas-holder without any great alteration of total pressure in the reaction bottle. It is hardly necessary to mention that any such alteration of pressure would tend to upset the equilibrium between the gas and liquid phases. Immediately after taking this sample of the gas, both the mercury reservoir as also the gas-holder were disconnected from the reaction bottle.

A sample of the filtered liquid was next required. It was in practice impossible to obtain this without exposing the liquid more or less to the atmosphere. Even if it were passed on to an otherwise closed filter successfully, which would not be easy of execution, the filtered liquid would be exposed to ordinary air containing a much lower partial pressure of  $\text{CO}_2$  than the liquid had been brought into equilibrium with. On the whole it was considered best, after much consideration and attempts to design specially suitable apparatus, to simply pour the muddy reaction fluid on to a good and large sized paper filter, one working as rapidly as the circumstances of the precipitate would admit, and to depend rather on rapidity of operation, and consequent limit of time, for avoidance of change in the composition of the liquid phase. The fluid was therefore simply poured on to a 15 cm. S.S. "white ribbon" filter paper, the supply being regulated so that the filter remained fairly full whilst the following specimens of filtered liquid were being taken. It may be mentioned that in no case, not even with the more concentrated solutions, was there any perceptible precipitate of  $\text{MgCO}_3$  in the filtered liquid until long after the portions had been taken for analysis.

*Methods of analysis.*—The first 5 to 10 c.c. of the filtrate was discarded. Then a suitable quantity was run directly from the funnel into a weighed Erlenmeyer flask and the stopper inserted. From this portion the amount of total  $\text{CO}_2$  was ascertained. Thirdly, another suitable quantity of filtrate was measured by a pipette into a beaker for subsequent titration, from which the amount of base was determined. The closed Erlenmeyer flask was now weighed. The stopper of the Erlenmeyer flask carried a tapped  $\text{HCl}$ -supply funnel as well as an outlet tube for gas (closed temporarily until attached to the condenser).

Considering the total  $\text{CO}_2$  first, sufficient hydrochloric acid was run into the solution to render it acid. The acid liquid was then cautiously raised to a boiling temperature. The outlet tube of the flask had been connected to an inverted condenser, which again was connected to  $\text{H}_2\text{SO}_4$  drying tubes and soda-lime tubes. The evolved  $\text{CO}_2$  was thus expelled from the reaction flask and finally brought into the soda-lime tubes in the usual manner. The "total"  $\text{CO}_2$  in the solution taken was thus ascertained.

The other quantity of filtered solution was titrated with standard  $\text{H}_2\text{SO}_4$ , methyl orange being employed as the indicator, from which the amount of  $\text{MgCO}_3$  could be deduced. The equivalent of this quantity is styled "combined"  $\text{CO}_2$  and the difference between this and the total  $\text{CO}_2$  is styled "free"  $\text{CO}_2$ .

In the case of the system  $\text{CaCO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  the amount of "free"  $\text{CO}_2$  is always largely in excess of the "combined"  $\text{CO}_2$  and the salt  $\text{Ca}(\text{HCO}_3)_2$  even if it really exists, can only do so in the presence of a considerable concentration of  $\text{H}_2\text{CO}_3$ . The corresponding magnesium salt is however very much more stable and the quantities of "combined" and "free"  $\text{CO}_2$  in solution within the limits of pressure and temperature which we have employed are nearly equal. These terms "free" and "combined"  $\text{CO}_2$  are merely a convenience.

The sample of gas in the Plimpton gas-holder was analysed for  $\text{CO}_2$  in the usual manner.

*Mode of expressing the results.*—Although the solution of  $\text{MgCO}_3 + \text{H}_2\text{CO}_3$  is so nearly one of  $\text{Mg}(\text{HCO}_3)_2$  it is simpler for practical purposes to express the concentration of  $\text{MgCO}_3$  and  $\text{CO}_2$  separately and to calculate each as a function of the partial pressure.

Therefore from the data obtained at each temperature the constants in the expression

$$C^n = k p$$

have been evaluated for  $\text{MgCO}_3$  and  $\text{CO}_2$  respectively. It was necessary here to bear in mind that  $\text{MgCO}_3$  is appreciably soluble in pure water. The published data vary somewhat; Treadwell and Reuter<sup>1</sup> found 19 m. grms., Cameron and Seidell<sup>2</sup> from 17 to 22 m.grms. per 100 c.c. For our purposes we took 20 m.grms. as being nearly correct. The formula then becomes:—

$$\log [C - 20] = \frac{\log k + \log p}{n}$$

$C$  = m. grms. per 100 c.c.

$p$  = %  $\text{CO}_2$  in gas phase.

On plotting the constants  $n$  and  $\log k$  against the temperature it was apparent that there were slight irregularities in them, and that better values would be obtained by assuming that each was a linear function of the temperature. The following final values for temperatures between  $20^\circ$  and  $40^\circ\text{C}$ . were then obtained by the method of least squares:—

For  $\text{MgCO}_3$ :

$$\log k = 4.24358 - .041049 t$$

$$n = 1.62098 - .0029114 t$$

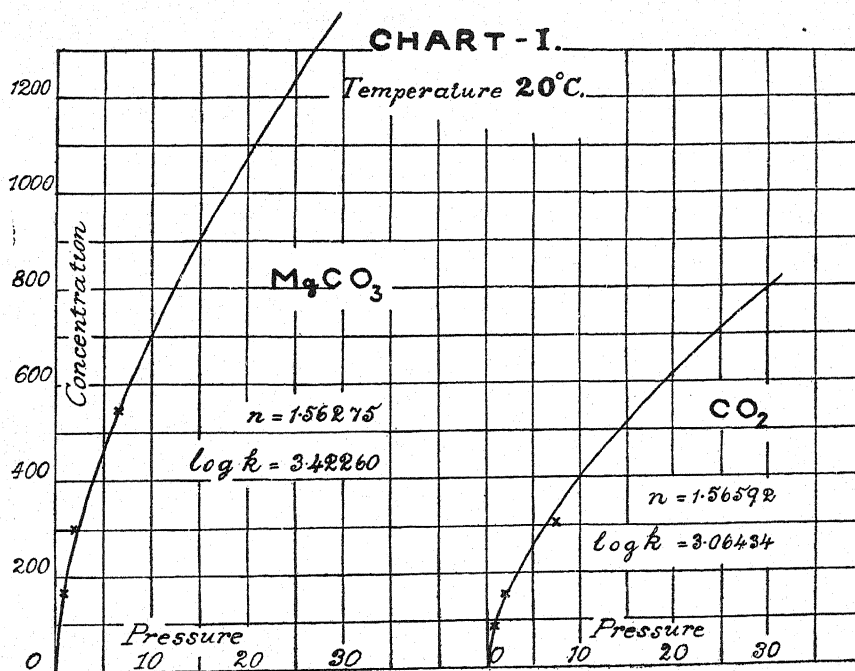
For  $\text{CO}_2$ :

$$\log k = 3.44718 - .019142 t$$

$$n = 1.42957 + .0068174 t$$

<sup>1</sup> *Zeits. anorg. Chemie*, 1898, Vol. 17, p. 200.

<sup>2</sup> *Jour. Phys. Chem.*, 1903, Vol. 7, p. 588.



Temperature 20°C.

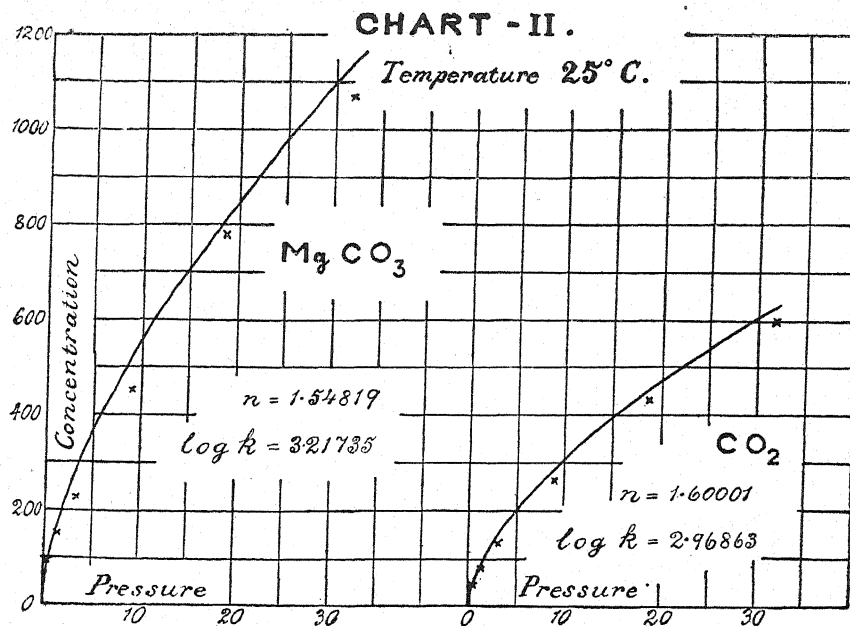
The subjoined statement shows the concentration of  $\text{MgCO}_3$  and  $\text{CO}_2$  as found and calculated for each experimental partial pressure of  $\text{CO}_2$  in the gas phase.

For  $\text{MgCO}_3$ ,  $n = 1.56275$ ,  $\log k = 3.42260$ .

„  $\text{CO}_2$ ,  $n = 1.56592$ ,  $\log k = 3.06434$ .

Statement I.

p.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
	$\text{MgCO}_3$		$\text{CO}_2$		$\text{MgCO}_3$		$\text{CO}_2$	
	found.	calculated.	found.	calculated.	found.	calculated.	found.	calculated.
% $\text{CO}_2$ in gas phase.								
9	165.6	164.8	84.8	84.7	35.5	35.3	34.7	34.6
2.1	302.4	269.1	149.2	145.5	64.8	57.7	61.0	59.5
6.6	544.8	538.3	300.4	302.2	116.8	115.4	122.9	123.6



Temperature 25°C.

The subjoined statement shows the concentration of  $\text{MgCO}_3$  and  $\text{CO}_2$  as found and calculated for each experimental partial pressure of  $\text{CO}_2$  in the gas phase.

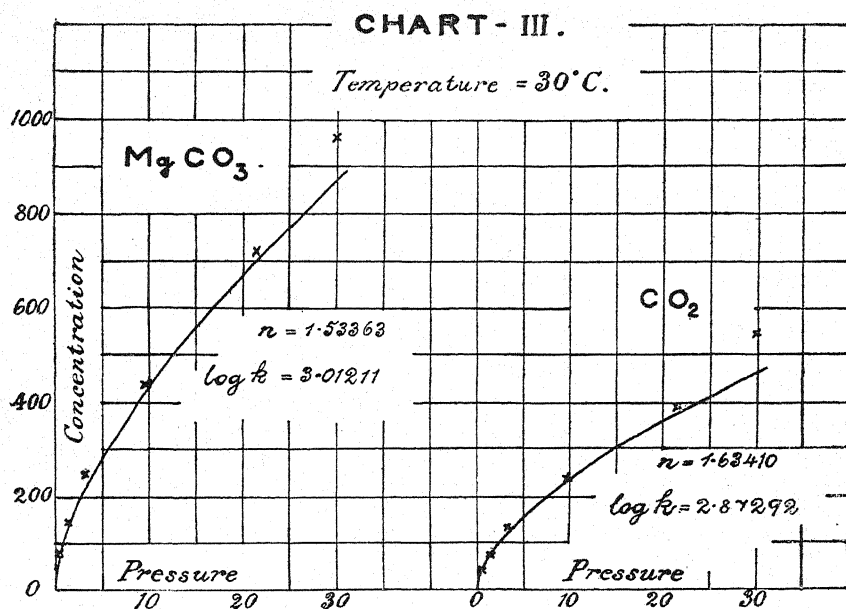
For  $\text{MgCO}_3$ ,  $n = 1.54819$ ,  $\log k = 3.21735$ .

„  $\text{CO}_2$ ,  $n = 1.60001$ ,  $\log k = 2.96863$ .

*Statement II.*

p.  % $\text{CO}_2$ in gas phase.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
	$\text{MgCO}_3$		$\text{CO}_2$		$\text{MgCO}_3$		$\text{CO}_2$	
	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.
.4	88.8	86.2	40.6	40.4	19.0	18.5	16.4	16.5
1.4	147.6	168.8	76.6	88.5	31.6	36.2	31.3	36.2
3.3	232.8	278.9	129.4	151.2	49.9	59.8	52.9	61.8
9.1	451.2	518.4	260.4	285.0	96.7	111.1	106.5	116.6
18.8	775.2	816.4	426.6	448.5	166.1	175.0	174.5	183.4
31.9	1062.0	1140.6	589.8	624.1	227.6	244.4	241.2	255.3





Temperature 30°C.

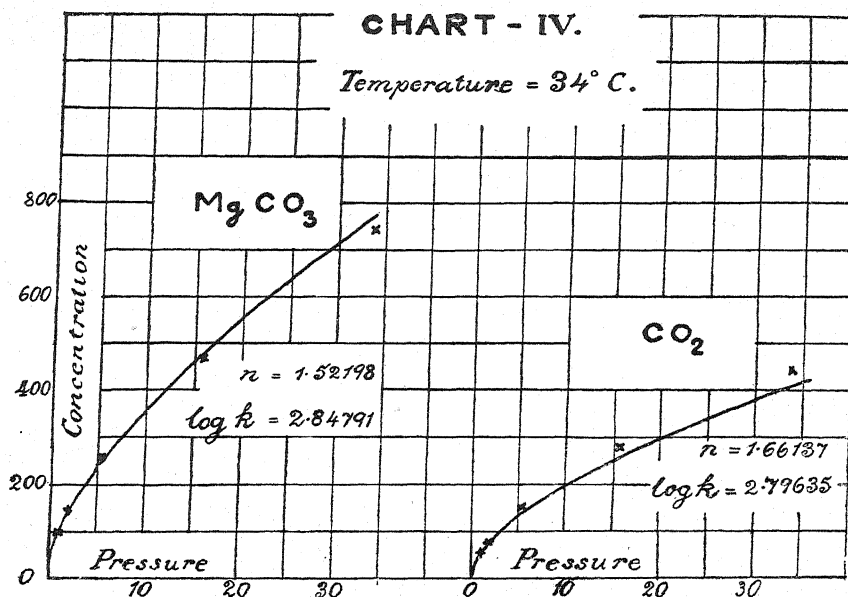
The subjoined statement shows the concentration of  $\text{MgCO}_3$  and  $\text{CO}_2$  as found and calculated for each experimental partial pressure of  $\text{CO}_2$  in the gas phase.

For  $\text{MgCO}_3$ ,  $n = 1.53363$ ,  $\log k = 3.01211$ .

„  $\text{CO}_2$ ,  $n = 1.63410$ ,  $\log k = 2.87292$ .

*Statement III.*

p.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
	$\text{MgCO}_3$		$\text{CO}_2$		$\text{MgCO}_3$		$\text{CO}_2$	
	found.	calcu- lated.	found	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.
% $\text{CO}_2$ in gas phase.								
·5	79·2	78·6	40·7	37·5	17·0	16·8	16·7	15·3
1·6	144·0	145·1	75·7	76·4	30·9	31·1	31·0	31·3
3·2	247·2	216·5	132·7	116·7	53·0	46·4	54·3	47·7
9·8	438·0	427·7	238·8	231·6	93·9	91·7	97·7	94·7
21·6	720·0	702·6	387·6	375·6	154·3	150·6	158·5	153·6
30·0	960·0	865·6	543·8	459·2	205·7	185·5	222·4	187·8



Temperature 34°C.

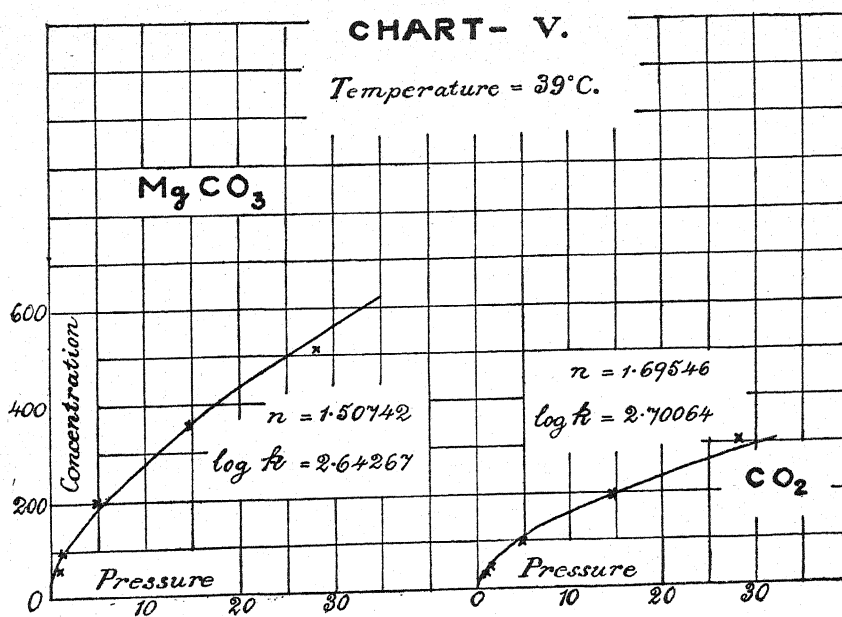
The subjoined statement shows the concentration of  $\text{MgCO}_3$  and  $\text{CO}_2$  as found and calculated for each experimental partial pressure of  $\text{CO}_2$  in the gas phase.

For  $\text{MgCO}_3$ ,  $n = 1.52198$ ,  $\log k = 2.84791$ .

„  $\text{CO}_2$ ,  $n = 1.66137$ ,  $\log k = 2.79635$ .

*Statement IV.*

p.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
	$\text{MgCO}_3$		$\text{CO}_2$		$\text{MgCO}_3$		$\text{CO}_2$	
	found.	calculated.	found.	calculated.	found.	calculated.	found.	calculated.
% $\text{CO}_2$ in gas phase.								
1.1	97.2	99.1	52.4	51.1	20.8	21.3	21.4	20.9
1.9	145.2	133.3	75.9	71.0	31.1	28.6	31.0	29.0
5.5	259.2	247.8	149.4	134.5	55.6	53.1	61.1	55.0
15.9	468.0	477.7	277.5	254.9	100.3	102.4	113.5	104.3
33.9	741.6	772.7	440.6	402.0	158.9	165.6	180.2	164.4
56.8	988.8	1076.5	568.2	548.4	211.9	230.7	232.4	224.3



The subjoined statement shows the concentration of  $\text{MgCO}_3$  and  $\text{CO}_2$  as found and calculated for each experimental partial pressure of  $\text{CO}_2$  in the gas phase.

For  $\text{MgCO}_3$ ,  $n = 1.50742$ ,  $\log k = 2.64267$ .

„  $\text{CO}_2$ ,  $n = 1.69546$ ,  $\log k = 2.70064$ .

Statement V.

p.	m. grms. per 100 c.c.				moles $\times 10^3$ per 100 moles water.			
	$\text{MgCO}_3$		$\text{CO}_2$		$\text{MgCO}_3$		$\text{CO}_2$	
	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.	found.	calcu- lated.
% $\text{CO}_2$ in gas phase.								
1.0	60.0	76.6	34.1	39.2	12.9	16.4	14.0	16.0
1.5	98.4	94.1	41.6	49.7	21.1	20.2	17.0	20.3
4.9	196.8	182.5	96.4	100.0	42.2	39.1	39.4	40.9
14.7	357.6	356.9	191.7	191.1	76.6	76.5	78.4	78.2
28.2	511.2	539.0	300.1	280.7	109.6	115.5	122.7	114.8
50.0	684.0	778.9	409.2	393.5	146.6	166.9	167.4	160.9

*Statement VI.—Calculated concentrations of  $\text{MgCO}_3$  and  $\text{CO}_2$   
(milligrams per 100 c.c.)*

p	20°C		25°C		30°C		34°C		39°C	
% $\text{CO}_2$ in gas phase	$\text{MgCO}_3$	$\text{CO}_2$	$\text{MgCO}_3$	$\text{CO}_2$	$\text{MgCO}_3$	$\text{CO}_2$	$\text{MgCO}_3$	$\text{CO}_2$	$\text{MgCO}_3$	$\text{CO}_2$
·5	119·4	58·2	96·5	46·5	78·6	37·5	67·2	31·8	55·8	26·0
1·0	174·9	90·6	139·7	71·7	112·1	57·3	94·3	48·2	76·6	39·2
2·0	261·4	141·0	207·3	110·5	164·6	87·6	137·2	73·2	109·7	58·9
3·0	333·4	182·6	263·4	142·4	208·4	112·2	173·0	93·4	137·4	74·9
4·0	396·2	219·5	313·1	170·5	247·3	133·8	204·8	111·1	162·1	88·7
5·0	453·9	253·1	358·5	196·0	282·9	153·4	234·0	127·0	184·7	101·2
10·0	696·1	394·0	549·7	302·3	433·1	234·5	357·5	192·8	280·9	152·3
15·0	896·4	510·5	708·3	389·4	558·2	300·5	460·5	246·1	361·4	193·4
20·0	1073·5	613·4	848·9	466·2	669·2	358·3	552·1	292·6	433·2	229·2
25·0	1235·2	707·3	977·4	535·9	770·9	410·8	636·2	334·7	499·2	261·4
30·0	1385·6	794·7	1097·0	600·6	865·7	459·2	714·6	373·5	560·8	291·1

*Summary in respect of this system.*

1. The concentration of solution of  $\text{Mg}(\text{HCO}_3)_2$  in respect of any specified partial pressure of  $\text{CO}_2$  is from 5 to 15 times greater than that of the corresponding calcium salt.

2. The ratio of  $\text{MgCO}_3 : \text{H}_2\text{CO}_3$  in the solution is much more nearly unimolecular than in the case of the calcium salt; in fact the solution contains only a slight excess of the quantity of  $\text{H}_2\text{CO}_3$  required by the bicarbonate formula.

3. The solution of  $\text{Mg}(\text{HCO}_3)_2$  is much more stable than that of the calcium salt.

4. Regarding the data obtained by others, Engel's<sup>1</sup> were obtained under so much higher pressures of  $\text{CO}_2$  — several atmospheres — that they are not comparable with ours. Treadwell and Reuter's<sup>2</sup> experiments, as was noticed in our memoir<sup>3</sup> on the calcium salt, were conducted under such imperfect conditions that supersaturation was to be expected.

<sup>1</sup> Engel and Ville, *Compt. Rend.*, Vol. 93, p. 340; Engel, *Ann. Chim. Phys.*, (6), Vol. 13, p. 349.

<sup>2</sup> *Zeits. anorg. Chem.*, Vol. 17, p. 200.

<sup>3</sup> *Mem. Dept. Agri. Ind.*, Chem. Ser., Vol. I, No. 7.

## PART II.

*The system  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ .*

This system has not so far as we are aware been previously examined, though experiments on the action of  $\text{H}_2\text{CO}_3$  on Dolomites have been made. The latter will be referred to subsequently. The system  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , is naturally very much more complicated than either of those which have been already discussed, and we have been unable to define it at all precisely.

A little consideration shows that if saturated solutions of the two bicarbonates, each in equilibrium with the same partial pressure of  $\text{CO}_2$  and at the same temperature, are mixed, a precipitation of  $\text{CaCO}_3$  must take place. For although the law of mass action probably would not hold in its entirety, still the *direction* of its effect must be that which this law would indicate. Thus it may not be quite true that the values of the constants

$$K_{\text{Ca}} = \frac{\text{Ca}^{++} \times (\text{HCO}_3')^2}{\text{Ca}(\text{HCO}_3)_2}$$

$$K_{\text{Mg}} = \frac{\text{Mg}^{++} \times \text{HCO}_3')^2}{\text{Mg}(\text{HCO}_3)_2}$$

will be, under the circumstances of a mixture of the solutions of the two salts, identical with those of the individual solutions. But it *is* to be expected that any large increase of  $\text{HCO}_3'$  ions in the mixed solution would cause a precipitation of  $\text{Ca}^{++}$ .

A solution of  $\text{Mg}(\text{HCO}_3)_2$  saturated for any specified condition of temperature and  $\text{CO}_2$  partial pressure is many times more concentrated than that of the calcium salt under like conditions. The

magnesium bicarbonate is not according to Bodländer,<sup>1</sup> nearly so completely hydrolysed as the calcium salt, but after making all allowances for this and other possible modifying influences, it has to be recognised that the concentration of  $\text{HCO}_3^-$  ions in the magnesium bicarbonate solution must be very much greater than in that of the calcium salt. Hence it follows that mixture of these solutions in equal volumes will cause a precipitation of  $\text{CaCO}_3$ .

One or two examples of this effect may be quoted, but before doing so a brief note must be made of the methods employed both for the attainment of equilibrium as also for the analytical determinations.

*Attainment of equilibrium.*—For some portion of the work the same apparatus was employed as for the magnesium bicarbonate investigation; but later, when it was found that the periods of time required for equilibrium probably extended to weeks, and that large quantities of solution would be required, the reactions were made in winchester bottles maintained in agitation on a revolving frame in a room the temperature of which did not vary by more than  $1^\circ\text{C}$ . for long periods. The latter arrangement did not admit of the mixtures being kept at specified temperatures as was readily possible in the former apparatus, but it was the best arrangement available and has yielded much information regarding the system. The materials were placed in the bottles and either a mixture of air and  $\text{CO}_2$  gas, previously prepared of specified proportions, passed into the bottle for such a time as would ensure that the gas phase was approximately that desired, or this was done after preliminary agitation. This displacement of the gas phase by a mixture of known composition was performed as frequently (every day, or every several days) as was found to be necessary in order that the composition of the gas phase should remain approximately what was desired. It was therefore necessary to

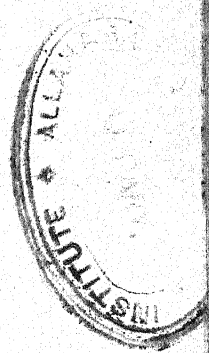
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<sup>1</sup> *Zeits. f. phys. Chemie*, XXXV, p. 27.



sample and analyse the gas phase frequently. Samples were withdrawn by attaching a stopper to the winchester which carried (i) an inlet tube opening in the bottle neck, (ii) an outlet tube opening near the surface of the liquid; the former was attached to the air +  $\text{CO}_2$  supply, the latter to the Plimpton gas-holder; hence on opening the connections, a sample of the gas from near the liquid was withdrawn, whilst an equal volume of air +  $\text{CO}_2$  was introduced near the stopper. Thus the pressure in the bottle was not materially altered and the gas withdrawn was not materially affected by that which flowed in. The amount of admixture of common air that would necessarily pass into the bottle neck when changing the ordinary stopper for the one carrying the tubes was naturally very small, too small to affect the gas phase materially and could not affect the sample which was withdrawn from a situation some inches below the neck.

*Methods of analysis.*—The determination of (a) the  $\text{CO}_2$  in the gas phase, (b) the total  $\text{CO}_2$  in the liquid phase, and (c) the total amount of base present require no explanation; these determinations were conducted in the same manner as when the magnesium salt alone was present. The estimations of  $\text{CaO}$  and  $\text{MgO}$  were made as follows:—The 100 c.c. which had been titrated with standard  $\text{H}_2\text{SO}_4$  for total base, was concentrated to about 20 c.c. and an equal volume of 99% ethyl alcohol was added together with one or two drops of dilute  $\text{H}_2\text{SO}_4$ . The  $\text{CaSO}_4$  was thus precipitated; the length of time required depended on the quantity of lime present; 24 hours was usually sufficient, but when there was less than about 10 m. grms., two days had to be allowed. The calcium sulphate was separated on a Gooch-asbestos filter and weighed as  $\text{CaSO}_4$  anhydrous. The error in this determination was about .5 m. grms. The alcoholic filtrate was evaporated cautiously on a sand bath until nearly dry, when the sulphuric acid charred the methyl orange; this residue was extracted with dilute  $\text{HCl}$  and the  $\text{MgO}$  was precipitated as phosphate. The error in this determination was about .5 m. gram.



*Statement VII.—Data obtained from mixtures of calcium and magnesium bicarbonate solutions.*

Examples of mixtures of equal volumes of the solutions.

Volume of $\text{Ca}(\text{HCO}_3)_2$ solution	..	..	100 c.c.	50 c.c.	25 c.c.
Volume of $\text{Mg}(\text{HCO}_3)_2$ solution	..	..	100 c.c.	50 c.c.	25 c.c.
Grams $\text{CaCO}_3$ in solution	..	..	0.0729	0.0364	0.182
Grams $\text{MgCO}_3$ in solution	..	..	1.5660	.7830	.3915
Total volume after diluting with water, if necessary	..	..	200 c.c.	200 c.c.	200 c.c.
Ratio Ca : Mg (molecular equivalents)	..	..	1 : 26	1 : 26	1 : 26
Period of agitation	..	..	7 days	7 days	7 days
Temperature	..	..	29—30°C.	29—30°C.	29—30°C.
p = % $\text{CO}_2$ in gas phase after shaking for seven days	..	..	18.0	6.7	2.3
			milligrams per 100 c.c.		
$\text{CO}_2$ in solution—total	..	..	920.1	515.6	335.2
Do. " free "	..	..	524.1	245.9	153.4
Do. " combined "	..	..	396.0	269.7	181.8
Ca in terms of $\text{CO}_2$	..	..	.3	.1	.1
Equal to $\text{CaCO}_3$	..	..	.7	.2	.2
Mg in terms of $\text{CO}_2$	..	..	401.2	274.3	185.1
Equal to $\text{MgCO}_3$	..	..	762.3	521.2	351.7

NOTE.—" Combined "  $\text{CO}_2$  is that equivalent to normal carbonates; " free "  $\text{CO}_2$  is that in excess of " combined "  $\text{CO}_2$ .

In these experiments some  $\text{CaCO}_3$  and  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  was added to the mixtures at the commencement in order to have both solid phases present throughout. Although the agitation was stopped before equilibrium had set in, these experiments as well as a number of other similar ones, serve to demonstrate the fact that  $\text{CaCO}_3$  becomes practically insoluble in the presence of an excess of  $\text{Mg}(\text{HCO}_3)_2$  which is what was expected on theoretical grounds. Some work by Moressee,<sup>1</sup> in which calcium and magnesium oxides were treated with carbonic acid at 5—6 atmosphere pressure, yielded a corresponding result; the solution contained only magnesium carbonate. A like result was obtained by Pattinson.<sup>2</sup> Following these, a number of experiments were made to ascertain what concentration of  $\text{Mg}(\text{HCO}_3)_2$  may be present without causing a precipitation of  $\text{CaCO}_3$ .

<sup>1</sup> Cf. Cesaro, *Bull. Acad. Roy. Belg.*, 1910, 234—265; *Abs. Chem. Soc.*, 1910 (ii), 613

<sup>2</sup> *Chem. News*, 1863, 128.

## Statement VIII.

Experiment No.	1	2	3	4	5*	6	7*	8	9*	10	11	12*	13*	14
Grms. $\text{CaCO}_3$ in solution	1.098	1.072	1.098	1.072	.154	1.543	.154	1.464	.154	1.543	1.429	.154	.154	1.543
Grms. $\text{MgCO}_3$ in solution	5.535	5.400	3.690	3.600	.222	2.592	.233	1.230	.117	1.296	1.200	.058	.065	.048
Vol. in c.c. (after diluting with water)	1978	1992	1818	1832	216	2200	216	2106	208	2100	2110	204	204	2050
Ratio : Ca : Mg (molecular equivalents)	1 : 6	1 : 6	1 : 4	1 : 4	1 : 2	1 : 2	1 : 2	1 : 1	1 : 1	1 : 1	1 : 1	2 : 1	2 : 1	2 : 1
Period of agitation, days	7	7	7	7	8	7	7	7	7	7	7	7	8	7
Temperature	30°	30°	30°	30°	29°-30°	30°-31°	29°-30°	30°	29°-30°	30°-31°	30°	29°-30°	29°-30°	30°-31°
P = % $\text{CO}_2$ in gas phase when agitation stopped	10.6	3.1	11.3	1.5	10.2	6.2	13.2	11.4	11.9	8.5	3.9	12.9	10.8	8.2
milligrams per 100 c.c.														
$\text{CO}_2$ in solution—total	318.2	222.0	220.4	190.6	199.4	120.6	175.9	109.2	146.6	76.4	69.0	92.2	123.7	67.0
Do " " free "	170.2	82.4	111.0	79.5	97.5	59.0	90.4	70.6	54.6	38.7	37.3	52.2	66.3	39.7
Do " " combined "	148.0	139.6	109.4	111.1	101.9	61.6	85.5	38.6	92.0	37.7	31.7	40.0	57.4	27.3
Ca in terms of $\text{CO}_2$	Nil.	6	Nil.	.5	Nil.	.4	1.0	6.8	1.4	5.8	3.5	9.2	2.7	10.8
Equal to $\text{CaCO}_3$	..	1.4	..	1.1	..	.9	2.3	15.4	3.2	13.2	7.9	20.4	6.1	24.6
Mg in terms of $\text{CO}_2$	147.5	141.3	100.4	105.5	105.8	63.4	83.0	31.3	96.3	32.5	29.3	32.1	56.3	17.4
Equal to $\text{MgCO}_3$	280.2	268.5	190.8	206.4	201.0	120.5	157.7	59.5	183.0	61.7	55.7	61.0	107.0	33.1

Note.—"Combined"  $\text{CO}_2$  is that equivalent to normal carbonates; "free"  $\text{CO}_2$  is that in excess of "combined"  $\text{CO}_2$ .

Of the experiments referred to in this statement Nos. 5, 7, 9, 12 and 13 were conducted in the small bottles and agitating apparatus which were used for the magnesium carbonate system; the remainder were performed in winchester bottles at room temperature. It is improbable that in any of them a state of equilibrium had set in, but the main result was very definite, namely, that where a higher ratio of magnesium : calcium than 1 : 1 was employed, the latter was substantially all precipitated; where however the ratio was equal, definite, though small amounts of calcium remained in solution. In the experiments marked with asterisks an excess of  $\text{CaCO}_3$  and  $\text{MgCO}_3$  was added to the initial mixture; in all others only the perfectly clear solutions of the bicarbonates were employed. The latter are particularly interesting because not only was a crystalline precipitate formed, but the total amounts of lime and magnesia present in solution at the conclusion of each experiment were determined, and compared with the initially used quantities. These data are as set out in the subjoined statement.

*Statement IX.*

Experiment No.	Ratio Ca : Mg (molecular equivalents)	CaCO <sub>3</sub> grms.		MgCO <sub>3</sub> grms.	
		initial	remaining in solution	initial	remaining in solution
1	1 : 6	1.10	<i>Nil.</i>	5.54	5.59
2	1 : 6	1.07	.03	5.40	5.33
3	1 : 4	1.10	<i>Nil.</i>	3.69	3.73
4	1 : 4	1.07	.02	3.60	3.69
6	1 : 2	1.54	.02	2.59	2.64
10	1 : 1	1.54	.28	1.30	1.30
8	1 : 1	1.46	.33	1.23	1.25
11	1 : 1	1.43	.17	1.20	1.18
14	2 : 1	1.54	.50	.65	.68

There is thus no doubt that the magnesium carbonate remained in solution in every case, whilst the greater part of the calcium carbonate was precipitated. The crystalline precipitates were submitted to the Director of the Geological Survey, who very kindly had them examined. Owing to their minuteness there was some

doubt as to the identity of the crystalline forms, but there was little doubt that the precipitate obtained from mixture of the solutions in the ratio  $\text{Ca} : \text{Mg} = 2 : 1$  consisted of calcite, whilst those obtained from higher proportions of Mg were principally aragonite with subordinate quantities of calcite. The chemical analysis showed that the precipitates were in all cases pure  $\text{CaCO}_3$ . Regarding the concentrations of the salts in solution, in two instances (Experiments Nos. 2 and 4) the solution contained rather more magnesium carbonate than was to be expected from the partial pressure; each contained a small amount of calcium carbonate, but this fact could not well explain the excess of magnesium salt, which is no doubt due to simple supersaturation. In all other cases the concentration of  $\text{MgCO}_3$  was much below what would be expected in the absence of  $\text{CaCO}_3$ . In respect of calcium carbonate, the concentration was in every case much below that which would be expected in the absence of  $\text{MgCO}_3$ ; in experiments Nos. 12 and 14 the concentrations of  $\text{CaCO}_3$  most nearly approach what would be expected from the  $\text{CO}_2$  partial pressure, but even in these cases it was little more than one half of what would be present in the absence of  $\text{MgCO}_3$ . The amount of "free"  $\text{CO}_2$  should have approximated to or have been slightly in excess of the "combined"  $\text{CO}_2$  in all cases where all or most of the calcium carbonate had been precipitated, that is in experiments Nos. 1 to 7; in Nos. 2 and 4 the divergence is serious and these are the instances in which the solution was presumably supersaturated with respect to  $\text{MgCO}_3$ . In experiment No. 9 also the quantity of "free"  $\text{CO}_2$  was materially different from that which might be expected, which may again be an instance of supersaturation with respect to  $\text{MgCO}_3$  in the presence of  $\text{CaCO}_3$ .

Although these experiments with mixtures of calcium and magnesium bicarbonates were defective in that equilibrium had not set in, they serve the chief end in view, for they demonstrate very definitely that presence of an excess of magnesium carbonate renders calcium carbonate all but insoluble. Experiments Nos. 7,

9, 12 and 13 do not contradict this deduction, because although some magnesium carbonate was originally added to the mixture, it was only a small quantity and presumably all dissolved. Had there been any magnesium carbonate present in the solid phase at the conclusion of the experiments the amount of lime in solution would have been much less. The amount of magnesium carbonate is thus a controlling factor of the solubility of calcium carbonate in the presence of carbonic acid.

*The solubility of Dolomite in carbonic acid.*

One of the ultimate objects of these investigations had been a more accurate knowledge of the concentration of calcium and magnesium carbonates in the soil-aqueous solution, that is the solution as it actually exists in agricultural land, and it had become apparent that, apart from the presence of salts of other bases or of other salts of magnesium in material quantity, which as a matter of fact is an important restriction, no fertile soil could contain more than very nominal amounts of magnesium carbonate, for the presence of such would render the concentration of dissolved calcium carbonate so low as to interfere with the growth of crops. As an adjunct to this investigation, the effect of carbonic acid on dolomite deserved special consideration. The literature naturally contains many references to this subject.

- (i) Pattinson<sup>1</sup> found that dolomite yielded no  $\text{MgCO}_3$  in solution when treated with  $\text{H}_2\text{CO}_3$   $\text{H}_2\text{O}$ .
- (ii) Vesterberg,<sup>2</sup> Bischoff and Gorup-Besanez<sup>3</sup> found that dolomite behaves as a true double salt when treated with  $\text{H}_2\text{CO}_3$   $\text{H}_2\text{O}$ , though Bischoff also found that in some cases calcite is first removed from dolomitic limestone.
- (iii) Merrill<sup>4</sup> states that dolomite is much more stable than calcite.

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<sup>1</sup> *Chemical News*, 1863, p. 128; *Jour. Chem. Soc.*, Abs. 1882, 13.

<sup>2</sup> *Jour. Chem. Soc.*, 1903, Abs., ii, 302.

<sup>3</sup> *Jour. Chem. Soc.*, 1872, p. 59.

<sup>4</sup> "Rocks and Rock Weathering," p. 250.



- (iv) Philippi<sup>1</sup> found the calcium carbonate more readily removed than the magnesium salt, and Merrill states that calcareous rocks lose  $\text{CaCO}_3$  readily and that dolomite remains.
- (v) Roth<sup>2</sup> has shown that magnesite is sometimes removed more readily than calcite from dolomitic limestones.

These experiences are generally what one might anticipate. Three cases may be assumed :—

- (a) *Pure dolomite*.—If this is a true double salt as is generally believed, then on treatment with  $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$  the two carbonates would dissolve in equi-molecular proportions and an excess of  $\text{Mg}(\text{HCO}_3)_2$  could not occur in the solution so long at least as the conditions of temperature and pressure remained constant. The maximum concentration would be reached when the solution contained the maximum amount of  $\text{Ca}(\text{HCO}_3)_2$  which could exist in presence of  $\text{Mg}(\text{HCO}_3)_2$  and dolomite.
- (b) *Dolomitic limestone containing calcite*.—If the calcite is more readily soluble in  $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$  than dolomite, then such a limestone would tend to lose calcite and the dolomite would remain, though not necessarily unacted on.
- (c) *Dolomitic limestone containing magnesite*.—A precisely similar argument must hold in this case as in the last. If magnesite is the more soluble, the dolomite would remain, and in this case it could not pass into solution in any material quantity because the presence of  $\text{Mg}(\text{HCO}_3)_2$  would prevent any material quantity of  $\text{Ca}(\text{HCO}_3)_2$  from being in solution.

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<sup>1</sup> *Jour. Chem. Soc.*, 1899, *Abs.*, ii, 306.

<sup>2</sup> “*Rocks and Rock Weathering*,” p. 25.

For our experiments three specimens of dolomite were employed which are designated O, A and B. Specimen O was a white mineral from the neighbourhood of Nagpore ; A and B were nearly black minerals which Mr. R. G. Wells of the Tata Iron and Steel Company, Limited, very kindly sent us from Panposh. Their composition was found to be as follows :—

Dolomite.				O	A	B
Insoluble silicates and sand	..	..		1.15	2.83	6.35
Oxide of iron, &c. (ammonia ppt.)	..			.86	.49	.66
Lime	..	..	..	29.65	29.06	27.94
Magnesia	..	..	..	22.10	22.11	21.13
Carbonic acid	..	..	..	46.30	45.97	44.22
				100.06	100.46	100.30
Molecular ratio Ca : Mg	..	..	..	1 : 1.036	1 : 1.058	1 : 1.052

Each was pulverised finely and a portion which passed a brass sieve of 90 meshes to the inch was employed.

About 10—20 grms. in each case was placed in a winchester bottle with about 2000 c.c. distilled water and air + CO<sub>2</sub> passed in. The mixture was then agitated on a rotating machine continuously day and night in a room the temperature of which remained very constant. The initial effect of the agitation was naturally a reduction of the partial pressure of CO<sub>2</sub>. In order to obtain a specified partial pressure approximately, in any particular case, the required mixture of air + CO<sub>2</sub> was passed into the bottle in sufficient quantity to thoroughly displace that previously present. This alternate procedure of agitation and replacement of the gas phase was continued until the partial pressure of CO<sub>2</sub> remained approximately constant, after which the agitation was continued for some days.

*Statement X.—The data thus obtained are set out in the following :—*

No. of experiment.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure $\text{CO}_2$ % in gas phase.	m. grms. per 100 c.c.		moles $\times 10^2$ per 100 moles $\text{H}_2\text{O}$ .	
					$\text{CaCO}_3$	$\text{MgCO}_3$	$\text{CaCO}_3$	$\text{MgCO}_3$
1	O	33°	8	4.6	18.4	15.6	3.31	3.34
2	O	31°	6	12.6	20.4	12.9	3.68	2.78
3	O	30°	7	15.3	20.4	12.5	3.68	2.70
4	A	30°	9	6.3	8.6	13.1	1.55	2.82
5	B	30°	9	6.4	11.6	11.4	2.08	2.45
6	O	30°	250	1.3	16.8	12.0	3.02	2.58
7	A	30°	250	1.0	16.1	12.7	2.90	2.74
8	B	30°	250	.5	14.7	11.2	2.66	2.41
9	O	30°	13	4.6	5.9	5.3	1.06	1.15
10	A	30°	13	6.7	10.2	8.4	1.84	1.80

Although the ratio of calcium to magnesium as shown in the last two columns are not precisely 1 : 1 as would be expected for a solution of pure dolomite, they are so nearly so, especially considering the not very perfect conditions employed, that it cannot be doubted that each of these dolomites dissolved as a double salt. There is no evidence that the solution contained generally an excess of either carbonate. The concentrations of the solutions vary and are not proportional to the partial pressure of  $\text{CO}_2$ .

In one case, experiment No. 8, the concentration of the  $\text{Ca}(\text{HCO}_3)_2$  was approximately that required by the partial pressure of  $\text{CO}_2$  and in experiments Nos. 6 and 7 it approached that concentration, thus showing that it is possible at low partial pressures of  $\text{CO}_2$  to obtain a solution in contact with dolomite, which approximates to a concentration of  $\text{Ca}(\text{HCO}_3)_2$  equal to what would be obtained if calcium carbonate alone were the solid phase. But in all other instances the concentration was very much below this. In respect of  $\text{Mg}(\text{HCO}_3)_2$  the concentration of this salt was always far below what it would be if  $\text{MgCO}_3$  were the solid phase. Generally, dolomite appears to dissolve as such, but unlike either calcium or magnesium carbonates there is no sign that its solubility increases, above a certain concentration, with increase of partial pressure of  $\text{CO}_2$ . The long period of time allowed in these experiments renders this deduction undoubted.

*The effect of the presence of (a)  $\text{CaCO}_3$  or (b)  $\text{MgCO}_3$  with dolomite.*—Several experiments were made in which dolomite, plus marble or dolomite, plus  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  were treated with  $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$ ; other experiments were similarly made in which, to a solution of dolomite in  $\text{H}_2\text{CO}_3 + \text{H}_2\text{O}$  and containing an excess of dolomite,  $\text{CaCO}_3$  (precipitated) or  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  were added; again, in a third series, dolomite was added to a solution of calcium bicarbonate or magnesium bicarbonate. The data are exhibited in the subjoined statement.

*Statement XI.*

Experiment No.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure CO <sub>2</sub> % in gas phase.	m. grms. per 100 c.c.	
					CaCO <sub>3</sub>	MgCO <sub>3</sub>
1	O	30°	Dolomite, plus marble.		31.8	9.2
			9	12.5		
2	O	30°	Dolomite, plus MgCO <sub>3</sub> .3H <sub>2</sub> O.		Nil.	192.8
			9	3.0		
3	O	30°	Dolomite solution.		16.8	12.0
			250	1.3		
		30°	The same after addition of precipitated CaCO <sub>3</sub> .		18.8	11.6
			45	2.0		
4	B	30°	Dolomite solution.		14.7	11.2
			250	.5		
		30°	The same after addition of precipitated CaCO <sub>3</sub> .		35.6	10.4
			45	9.8		
5	O	30°	Dolomite solution.		5.9	5.3
			13	4.6		
		30°	The same after addition of precipitated CaCO <sub>3</sub> .		19.8	4.6
			4	4.4		

## Statement XI—contd.

Experiment No.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure CO <sub>2</sub> % in gas phase.	m. grms. per 100 c.c.	
					CaCO <sub>3</sub>	MgCO <sub>3</sub>
6	A	Dolomite solution.				
		30°	13	6.7	10.2	8.4
		The same after addition of precipitated CaCO <sub>3</sub>				
7	A	30°	4	6.1	28.0	6.9
		Dolomite solution.				
		30°	250	1.0	16.1	12.7
8	A	The same after addition of MgCO <sub>3</sub> .3H <sub>2</sub> O				
		30°	28	.6	4.1	20.4
		Dolomite solution.				
9	....	30°	250	1.0	16.1	12.7
		The same after addition of MgCO <sub>3</sub> .3H <sub>2</sub> O				
		30°	45	.9	9.5	42.2
10	O	Calcium bicarbonate solution.				
		....	....	....	40.7	....
		The same after addition of dolomite.				
11	....	28°	11	10.9	45.5	2.3
		Calcium bicarbonate solution.				
		....	....	....	40.7	....
12	O	The same, plus Dolomite and CaCO <sub>3</sub>				
		28°	11	11.2	45.9	.8
		Calcium bicarbonate solution.				
13	....	....	....	14.8	50.0	....
		The same, plus dolomite.				
		25°	9	14.0	45.5	1.5
14	O	Calcium bicarbonate solution.				
		....	....	....	16.2	....
		The same, plus dolomite.				
15	O	28°	13	1.4	18.4	1.5

*Statement XI—concl'd.*

Experiment No.	Variety of Dolomite.	Temperature.	Period of agitation, days.	Partial pressure $\text{CO}_2$ % in gas phase.	m. grms. per 100 c.c.	
					$\text{CaCO}_3$	$\text{MgCO}_3$
13	....	....	....	..	....	379.9
	O	28°	13	10.0	Nil.	379.9
14	....	....	....	....	....	352.3
	O	23°	7	9.0	Nil.	349.6

A consideration of the data of experiment No. 1 shows that the presence of marble does not prevent the carbonic acid attacking the dolomite, though the concentration of  $\text{Mg}(\text{HCO}_3)_2$  in the solution is distinctly less than we have found in the absence of calcium carbonate. Experiment No. 2 in which a large amount of  $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$  was present shows how completely this salt prevents the solution of the dolomite, for the amount of  $\text{Ca}(\text{HCO}_3)_2$  in solution was too small to detect. In other experiments only small amounts of the  $\text{CaCO}_3$  or  $\text{MgCO}_3$  respectively were added. In Nos. 3 and 4 a comparison of the quantities of  $\text{CaCO}_3$  added and subsequently found in solution, showed that all the  $\text{CaCO}_3$  had dissolved, whereas in Nos. 5 and 6 there was still a small amount of calcium carbonate in the solid state. There seems to have been in each case a small but measurable precipitation of magnesium carbonate. In experiments Nos. 7 and 8 only small amounts of  $\text{MgCO}_3$  were added and in No. 8 the whole dissolved; the corresponding data for No. 7 were not obtained. Finally experiments Nos. 9 to 14 show again that the presence of calcium bicarbonate largely protects dolomite from the solvent action of carbonic acid, whilst magnesium bicarbonate protects it entirely. It is evident then that  $\text{CaCO}_3$  will readily dissolve in a solution of dolomite in the



presence of  $\text{H}_2\text{CO}_3$ , without greatly altering the concentration of the  $\text{Mg}(\text{HCO}_3)_2$ ; on the other hand, when  $\text{MgCO}_3$  is dissolved in a solution of dolomite under corresponding conditions, the calcium carbonate of the dolomite becomes precipitated either partly or wholly according to the excess of  $\text{Mg}(\text{HCO}_3)_2$  in solution. These experiments confirm fully the anticipations which are set out on page 227.

*The "lime-magnesia ratio" in Soils.*

Indirectly this investigation offers some explanation of the somewhat contradictory results which have been obtained at experiment stations in different countries regarding the lime-magnesia ratios in soils.

Briefly, these experiments have usually shown that considerable excess of lime, in the form of the carbonate, may be employed without harm, whereas any considerable application of magnesium carbonate has usually proved harmful. Moreover, no fixed proportion of Ca : Mg has been generally found the best, but nearly all experiments show that the proportion of lime should largely exceed that of magnesia.

In the first place, it is to be realised that if, in the soil aqueous solution, there were any calcium sulphate or chloride, either would react with magnesium carbonate.<sup>1</sup> For example, in many experiments magnesium carbonate has been added to soils to which fertilisers, *e.g.*, ammonium salts or superphosphate have also been added, and in such cases more or less of the magnesium carbonate must have been changed to a more soluble salt, but unchanged magnesium carbonate must also have tended to render calcium carbonate insoluble. In the case of dolomitic limestone, the solubility of the calcium carbonate would probably not be reduced sufficiently to affect plant growth and this explains why such limestone has frequently proved serviceable. But where magnesium carbonate has been employed in any large quantity, its presence

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<sup>1</sup> Bottomley, *Jour. Chem. Soc., Trans.*, 1893, p. 696.

in the soil might easily reduce the solubility of calcium carbonate sufficiently to cause "lime-starvation."

*Summary in respect of the system  $\text{CaCO}_3$ ,  $\text{MgCO}_3$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{H}_2\text{O}$ .*

1. If a mixture of calcium and magnesium carbonates is subjected to the action of carbonic acid and water, the calcium carbonate is largely or wholly prevented from dissolving, a fact which is in accordance with the indication of the law of mass action.
2. Dolomite has been found by us, as by others, to dissolve in carbonic acid as such, but so far as we could ascertain the concentration does not depend only on that of the carbonic acid.
3. Dolomite is protected from the action of carbonic acid to a great extent by the presence of calcium carbonate, and magnesium carbonate protects it completely.
4. The addition of calcium carbonate to a solution of dolomite in presence of excess of carbonic acid seems to cause a slight precipitation of magnesium carbonate, but no explanation of this can be offered.
5. If magnesium carbonate is added in any material quantity to agricultural land, it may readily cause an almost entire precipitation of calcium carbonate and hence render the soil infertile. This fact probably explains in part the crop failure which has so often accompanied the application of magnesium carbonate to land in experiments on Loew's "lime-magnesia ratio."

## PREFACE.

Mr. A. G. Birt, Deputy Director of Agriculture, Assam, has been throughout jointly responsible for all the field work described or alluded to in this paper.

He modestly refuses to allow his name to appear as co-author, and I take this opportunity of expressing my thanks to him for assistance and advice always freely given; without it the work would have been impossible.

JORHAT, ASSAM, }  
*March 1st, 1914.* }

A. A. MEGGITT.

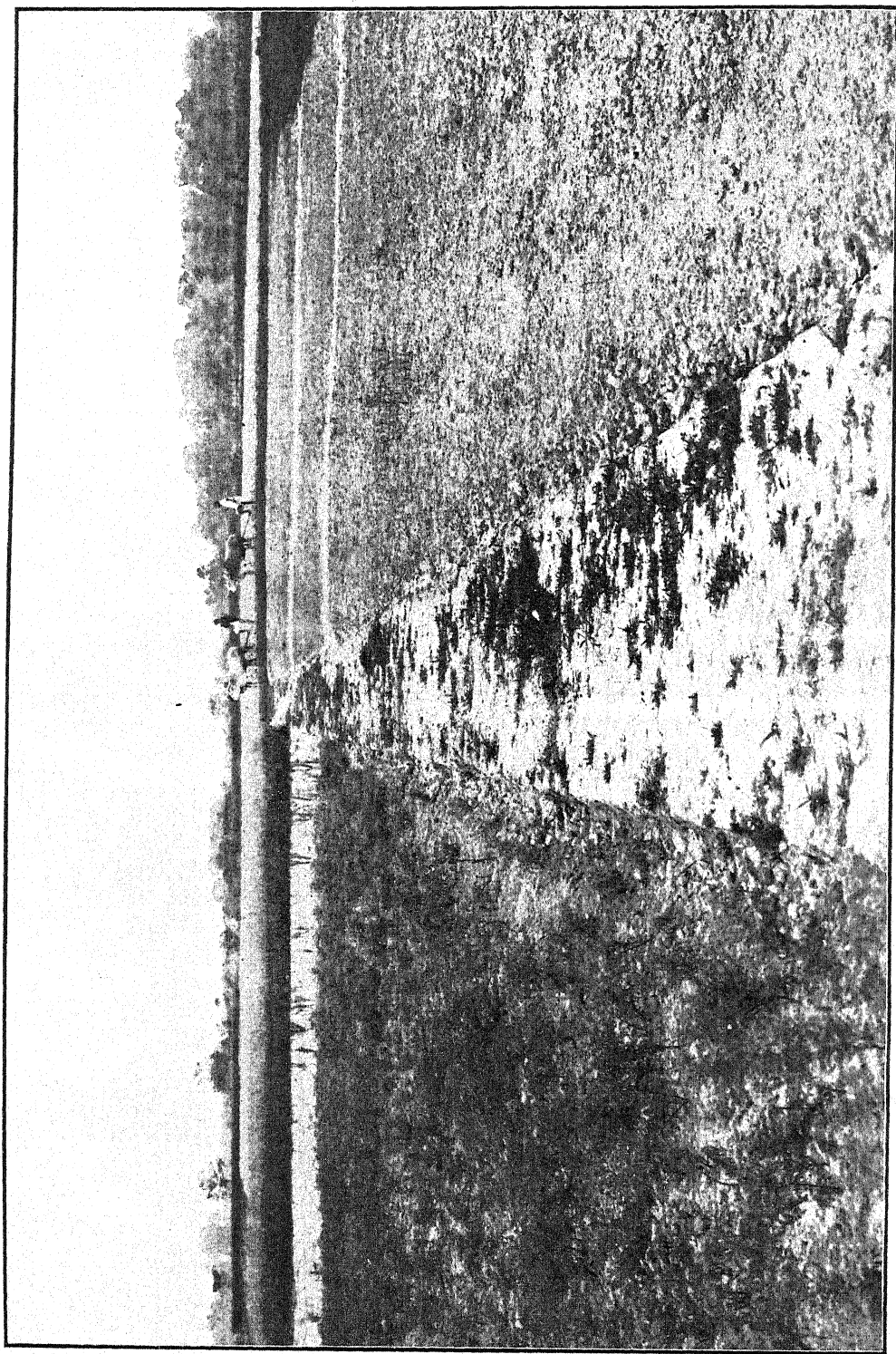
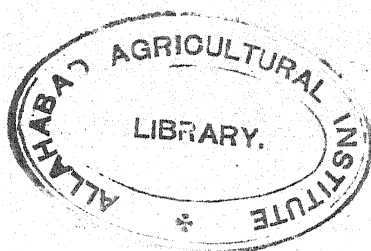


Photo-Engraved & printed at the Offices of the Survey of India, Calcutta, 1914.

JORHAT FARM. BLOCK G.

The plots on the left were limed, those on the right unlimed; treatment is otherwise identical. Oats and Gram were sown across both areas. Observe the standing crops of both on the limed side, and the absolute failure on the other.



## STUDIES OF AN ACID SOIL IN ASSAM

BY

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### INTRODUCTORY.

THE following pages contain some account of field and other work done on the old alluvium at the Government Farm, Jorhat, undertaken primarily with a view to ascertain, if possible, to what particular function of lime its observed early remarkably beneficial action on cropping there may be due.

Work on the liming problem has been going on since 1908 on this Farm.

It originated in the repeated failure of certain crops to survive the seedling stage during the *rabi* season even though well manured before sowing, and with no lack of soil moisture; the case was further aggravated in one instance by the fact that a green manure crop had been grown and ploughed in the previous rains, by way of preparation.

A full account of our early observations and work undertaken, will be found in the *Annual Report of the Jorhat Agricultural Experiment Station* for the year ending June 30th, 1912, pages 18-32. This is continued in the report of the same station for the year 1912-1913, pages 15-24. In these reports it is shown how after the application of lime several crops now grow much more luxuriantly, while others, *e.g.*, oats, gram, barley, mustard, linseed, jowar (*Andropogon Sorghum*), etc., which failed heretofore to outlive the seedling stage, now mature their crops normally.

An account of the further experiments laid down to study other aspects of manuring in relation to the liming problem is given in the same reports. Data in regard to the chemical and mechanical composition of the soil will be found in the Appendix.

Previous to being taken over by the Agricultural Department the land had been out of cultivation for many years ; it was covered by short scrub jungle and very coarse grass, and was used solely for grazing purposes.

The soil is very old alluvium and is a light loam lying over a compact reddish yellow sandy subsoil.

The surface soil is shallow, from 3 to 6 inches deep, fairly retentive of moisture and in good physical condition.

The subsoil is redder, and very deficient in organic matter, which combined with the fact that it has not been disturbed for very many years makes its physical condition temporarily poor.

The soil drains fairly readily.

The surface and subsoils are fairly sharply divided in the field, but are essentially the same in chemical and mechanical composition, the surface soil having become darker in colour and ameliorated by cultivation and incorporation with organic matter. The mechanical analysis shows that both soils are essentially very similar, about 80% of either falling in the fine sand and silt grades, only relatively small quantities of the clay fraction being present.

The soil is acid in reaction and very deficient in carbonate of lime.

Phosphoric acid is low both as to total and available supplies. There is thus a real as opposed to a mere temporary lack in respect of this element of plant-food.

This lack of phosphoric acid is probably aggravated by the absence of sufficiently large amounts of carbonate of lime and humus, high percentages of which may, and often do, offset a smaller percentage of phosphoric acid.



Of potash there is no dearth, and there would appear to be no immediate need for special potash manuring.

The amount of organic matter in the surface soil is possibly greater than obtains in many Indian soils, but there can be no doubt that a light soil of this character will be much improved by an increase in humus content. A good deal of the organic matter present consists probably of old residue of little value. Green manuring with cowpea has improved the soil enormously of recent years. The percentage of nitrogen present in the surface soil is what would normally be considered a fair one, but in view of the absence in anything like adequate quantity of carbonate of lime, conditions for nitrification are not as favourable as they might be, and an increase in the amount of nitrogen is indicated as desirable.

As to maximum saturation capacity this soil agrees well with figures quoted for similar soils in Europe; the figures suggest that the optimum proportion of water for the growth of the plant is some 13-16%.

The values for minimum saturation capacity are lower than those cited (Hall, *The Soil*, page 69) for similar soils in England, and this is probably due to the lower humus content of our soils. The hygroscopic capacity is low, and suggests the power of the soil to give up its moisture freely to crops in dry periods.

As previously explained the outstanding feature of our early experiments was the extraordinary effect of lime. Without it many crops could not be induced to survive even the seedling stage; after liming they were easily matured. (See Frontispiece.)

The question naturally arose as to why lime acts in this marked way. The reasons might be found in a number of possible causes of a physical, purely chemical, bio-chemical, biological and physiological nature; some of these aspects merge into one another and are very closely related, and are moreover imperfectly understood at present, so that it were futile to attempt any fine discrimination.

The soil is distinctly not of the type one usually associates with adverse physical conditions, or one upon which one would expect lime to confer much physical benefit perhaps. A good tilth and seed bed is easily obtained, the soil is naturally fairly retentive of moisture, the rainfall is high (80-90 inches) and well distributed, some rain falling nearly every month of the year. Knowing the soil one would not readily ascribe any considerable part of the action of lime to physical changes (a).

One of the very earliest actions of lime is a purely chemical one, which it exercises merely by virtue of its power to neutralise acids. So much lime is required by this soil to satisfy its various requirements that a dressing of 2 tons slaked lime per acre causes but a very slight and temporary increase in the percentage of calcium carbonate in the surface soil, as is clearly shown by the following figures :—

			3 months after liming.		18 months after liming.	
			%CaCO <sub>3</sub>	Reaction	% CaCO <sub>3</sub>	Reaction.
0 Lime plot	0 — 3" ..		0.02	Acid	0.02	Acid
	3 — 6" ..		0.015	"	0.015	"
30 maunds Lime plot (1 ton)	0 — 3" ..		0.04	Fairly alkaline	0.02	"
	3 — 6" ..		0.02	Acid	0.02	"
60 maunds Lime plot (2 tons)	0 — 3" ..		0.11	Strongly alkaline	0.02	Slightly alkaline.
	3 — 6" ..		0.015	Acid	0.015	Neutral.

These results shed some light on the question as to the quantity of lime which will be required to establish even a small working reserve of carbonate of lime in the surface soil.

(a) On stiffer soils the physical changes would, no doubt, be of much greater moment. Thus work on the old alluvium at Dacca has shown that while the use of lime there reduces the amount of the clay fraction (< 0.002 m.m. diam.), presumably by flocculation into larger aggregates from about 17 to 13% in a water sedimentation, at Jorhat so far this is not so, the limed and unlimed surface soils returning identical figures. There is, however, experimental evidence that deeper down in the Jorhat soil, some flocculation does take place as a result of applying lime to the surface.

A good deal of the added lime combines with acid organic compounds present, neutralising and fixing them, as is shown by the fact that whereas the unlimed soil gives up its humus to dilute ammonia quite readily yielding a dark brown solution, after liming it only does so after a preliminary weak acid digestion to break up the lime compounds formed.

Schloesing<sup>1</sup> has ascribed valuable physical properties to these so called calcium humates in certain soils. Working with silicious sand he found that "1% humic acid in the form of calcium humate had as great a cementing power as 11% of plastic clay."

Soils contain other colloid bodies than clay; amongst these are humus, hydrated ferric and aluminic oxides, hydrated silicic acid, and hydrated acid silicates, the latter accounting no doubt partly for the acidity of soils which are strongly acid and withall deficient in humus.

Possible interaction of lime with some of these colloidal substances, *e.g.*, a reaction with hydrous acid silicates, coupled perhaps with dehydration where quicklime is used—whereby may result non-colloidal anhydrous silicates—might conceivably modify the properties of the soil (*a*). Hence it is possible that lime may affect this soil physically and thereby alter its power to supply moisture to the plant. However from the fact that in the absence of lime some crops, *e.g.*, *matikalai* (*Phaseolus mungo*) do grow even in the *rabi* season and make some sort of a crop, while most others, *e.g.*, oats, gram, etc., sown at the same time die as seedlings (though examination has always disclosed the presence of sufficient soil moisture in the latter case), also the fact that seeds germinate apparently as well before as after liming, and again *jowar* sown in

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<sup>1</sup> Warington. *Physical Properties of Soil*, p. 27.

(*a*) Indications are not wanting that heavy liming may have an influence on the stiffness of straw of cereals, which is possibly connected with changes in the silica compounds of the soil. Analytical data to hand point to variations in silica content of the straw from limed and unlimed areas, but in the absence of information as to the probable extent of the variation in silica content of a given sample of straw from one and the same plot, and until further analytical data are to hand, it were futile to attempt to draw any conclusions. This part of the problem will probably require very special methods of investigation.

the rains always succumbs in the absence of lime, it seems to be reasonably clear that the failure of certain crops to survive is not due to any lack of soil moisture, and further the marked action of lime is not to be sought in modified water relationships as between soil and crop.

Added lime might function as a direct source of plant-food in respect of the element calcium, or by liberating other foods from the soil's reserves. It is very difficult to believe that the soil does not contain sufficient lime compounds to serve fully the requirements of crops for this element. Few soils do not. Were any large part of its effect due to its acting as a direct source of plant-food, then a dressing of 1 ton per acre would surely supply all that was necessary, and yet in the case of *jowar* a much bigger crop resulted from the application of 2 tons per acre.

O. Loew has attached great importance from a physiological standpoint to the presence in the soil of lime and magnesia in certain definite ratios for various crops. The results of our experiments do not at all connect the value of lime with any such relationship.

The beneficial action of lime may be found in its power of destroying by oxidation, or otherwise, directly or indirectly, noxious organic soil compounds; possibly preventing their formation, or at any rate their accumulation.

Some of these toxic substances are themselves acids, *e.g.*, the hydroxystearic acids isolated from certain infertile soils by Schreiner and his associates. Schreiner and Reed<sup>1</sup> have shown that "the maintenance of the most favourable soil conditions requires the oxidation of the organic soil constituents to a comparatively high state of oxidation."

They draw the further conclusion from their work, that though plant roots themselves are able to oxidise a certain amount of deleterious organic material, their power to do so may be entirely inhibited in the presence of excess of toxic material, but that lime salts increase the amount of oxidation possible in the latter case.

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<sup>1</sup> Bulletin 56. Bureau of Soils, U. S. Dept. of Agriculture.

Again they conclude that "the process of oxidation by roots is largely, if not entirely, due to the activity of a peroxidase produced by the roots. This oxidising enzyme is most active in neutral or slightly alkaline solutions and may be inhibited by the presence of acid."

Laboratory examination of the Jorhat soil had already disclosed positively the presence of an acid organic compound, definitely toxic to *jowar* seedling plants in extremely dilute culture solution (30 parts per million), the toxicity of which was partly or wholly negated by the addition of a complete nutrient solution containing nitric nitrogen, or by the addition of lime to neutrality. (Plate V.) The observations thus made in culture solution agree exactly with field results, and render it reasonably clear that the soil's infertility to certain cropping is due in no small part to the presence of toxic organic material. More recent work has proved that this body is not only non-toxic to transplanted paddy seedlings, but that it appears actually to favour their development in such concentrations as were definitely toxic to *jowar*. That this toxin is an actual constituent of the soil, and is not rather a compound formed during the process adopted for its isolation, is clearly proved by the fact that a water extract of the soil was itself quite toxic to *jowar* seedlings.

Further, examined by the method of Raciborski<sup>1</sup>, using phenolphthalin as indicator, the author has been able to show that the presence of this toxic body in solution does actually lead to a diminution of the root oxidising power as measured by the rate of oxidation of phenolphthalin to phenolphthalein.

Considered from the biological point of view the presence of noxious organic material in the soil besides being toxic to the plant itself, must also be inimical to many forms of bacterial life.

The presence of acidity in any form is contrary to the best functioning of certain normal soil micro-organisms which depend for their proper action upon the presence of a sufficiency of basic

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<sup>1</sup> *Bul. Acad. Sci. Cracovie, math.-nat.* Cl. 1905, 338.

ingredients. By its power then of neutralising acidity and its action on toxic soil material, whereby the soil becomes a suitable culture medium for a normal bacteriological flora, lime would stimulate bacterial activity leading to that marked improvement in the growth and colour of crops which has all along followed its use in our experience.

The chemical examination of the soil and the early field observations and cropping results led us to believe that the fault in the soil was due to a definite lack of basic constituents, to which the presence of toxic compounds, which may partly or wholly give rise to the acid condition, is attributable.

It seemed likely then on general grounds that the early beneficial action of added lime was primarily due to its supplying the base necessary for the neutralisation of the soil acids, some of them toxic, and to its power to bring about such other changes in the bio-chemical soil factor as results in the destruction of toxic organic compounds, whether by micro-organisms, enzymes or other vital agencies, and in checking their future formation, or in any case their accumulation to the danger point in the soil.

### EXPERIMENTAL.

A field experiment comprising some 52 small sub-plots was, therefore, commenced in the hope of throwing more light on some of the points raised in the introduction, and in order to fine down the possible reasons for its early beneficial action. It was considered far more satisfactory to carry out the work on small field plots, rather than in pots; an experiment carried out in tubs has proved that for the purposes of this investigation, tests so conducted in no wise approximate to field conditions, and give wholly irregular results. The scheme provides for the testing of each individual treatment with and also without lime.

Various alkali plots were included, *e.g.*, sodium carbonate, magnesium carbonate and potassium carbonate, to compare with the plot receiving lime only, another getting finely ground limestone.



Other two plots were given calcium sulphate and chloride respectively, to test the direct plant-food theory.

The three nitrates of potassium, sodium and lime were each separately used with a view to seeing whether the supply of readily assimilable nitrogen alone has any effect on cropping, in the absence of first neutralising part or the whole of the soil acidity.

Two further plots received sulphate and muriate of potash respectively, supplying soluble potash in the same amount as provided for in one of the plots manured with carbonate of potash.

The experiment was also designed to show how the use of certain acid or physiologically acid manures in the absence of liming is limited by the small amount of carbonate of lime present in the soil. Sulphate of ammonia alone and in combination with other manures enters into the scheme, and again plots are included where-on acid and basic forms of phosphoric acid are applied.

Besides those plots which receive either potash or nitrogen or phosphoric acid only, there will be found other plots manured with both potash (as sulphate) and also nitrogen, either as sodium nitrate or sulphate of ammonia ; others getting superphosphate in addition to the above combinations ; again, others receiving superphosphate in addition to one or other form of soluble nitrogen ; and finally one plot with superphosphate and sulphate of potash in the absence of nitrogen in any form.

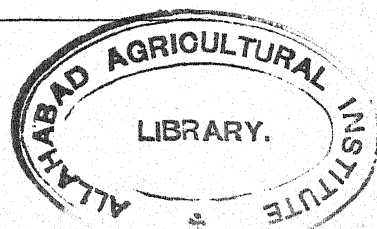
All the above combinations were applied with and without previous liming, and may serve to indicate the relative importance of one or other kind of plant-food in the economy of this soil.

The whole scheme will be readily grasped by referring to the plan of the experiment, Fig. I, and table of manuring, Table I.

The middle area A B C D was limed at the rate of 30 maunds per acre.\* There are thus 26 plots, each of 1/100 acre, the inner half of each being limed.

A B and D C represent dividing lines of bricks between the limed and unlimed half of each plot.

\* 30 Maunds = 1 ton approx.



Each plot was separated from those on either side of it by a 3 feet division.

TABLE I.

The manuring of the various plots was as follows :—

Plot.	Manure used.	Rate per acre.	REMARKS.
1 & 1a.	Ground limestone .. ..	30 mds.	
2 & 2a.	Sodium carbonate. Monohydrate .. ..	1,000 lbs.	Equal to 10 mds. slaked lime in neutralising power.
3 & 3a.	Do. do. .. ..	500 "	Equal to 5 mds. do.
4 & 4a.	No manure. .. ..		
5 & 5a.	Magnesium carbonate .. ..	1,000 "	Equal to 15 mds. lime in neutralising power.
6 & 6a.	Potassium do. .. ..	328 "	
7 & 7a.	Potassium carbonate .. ..	164 "	Containing potash equal to that supplied in 2 cwt. sulphate of potash on plots 18 & 18a.
8 & 8a.	Flour phosphate .. ..	600 "	Equal in money value to the basic slag used on plots 9 & 9a.
9 & 9a.	Basic slag .. ..	400 "	Supplying 80 lbs. $P_2O_5$ per acre.
10 & 10a.	Superphosphate. Concentrated .. ..	200 "	Supplying 80 lbs. sol. $P_2O_5$ per acre.
11 & 11a.	Sulphate of ammonia .. ..	250 "	Supplying 50 lbs. nitrogen per acre.
12 & 12a.	Sulphate of lime .. ..	4000 "	Containing approx. same amount of lime as 30 mds. slaked lime.
13 & 13a.	Calcium chloride .. ..	1000 "	Adding same amount of calcium as exists in 10 mds. lime approx.
14 & 14a.	Sodium nitrate .. ..	322 "	Supplying 50 lbs. nitrogen per acre.
15 & 15a.	Potassium nitrate .. ..	384 "	Do. do.
16 & 16a.	Calcium .. ..	384 "	Do. do.
17 & 17a.	Muriate of potash .. ..	224 "	
18 & 18a.	Sulphate of .. ..	224 "	Supplying same amount of potash as supplied by carbonate of potash in plots 7 & 7a.
19 & 19a.	No manure. .. ..		
20 & 20a.	Sodium nitrate .. ..	322 "	
	Superphosphate .. ..	200 "	
	Sulphate of potash .. ..	100 "	
21 & 21a.	Sulphate of ammonia .. ..	250 "	Superphosphate supplied 80 lbs. phosphoric acid per acre.
	Superphosphate .. ..	200 "	
	Sulphate of potash .. ..	100 "	
22 & 22a.	Sodium nitrate .. ..	322 "	Sulphate of potash 50 lbs. potash per acre.
	Superphosphate .. ..	200 "	
23 & 23a.	Sulphate of ammonia .. ..	250 "	Nitrate of soda 50 lbs. nitrogen per acre.
	Superphosphate .. ..	200 "	
24 & 24a.	Sodium nitrate .. ..	322 "	Sulphate of ammonia 50 lbs. nitrogen per acre.
	Sulphate of potash .. ..	100 "	
25 & 25a.	Sulphate of ammonia .. ..	250 "	
	Sulphate of potash .. ..	100 "	
26 & 26a.	Sulphate of potash .. ..	100 "	
	Superphosphate .. ..	200 "	

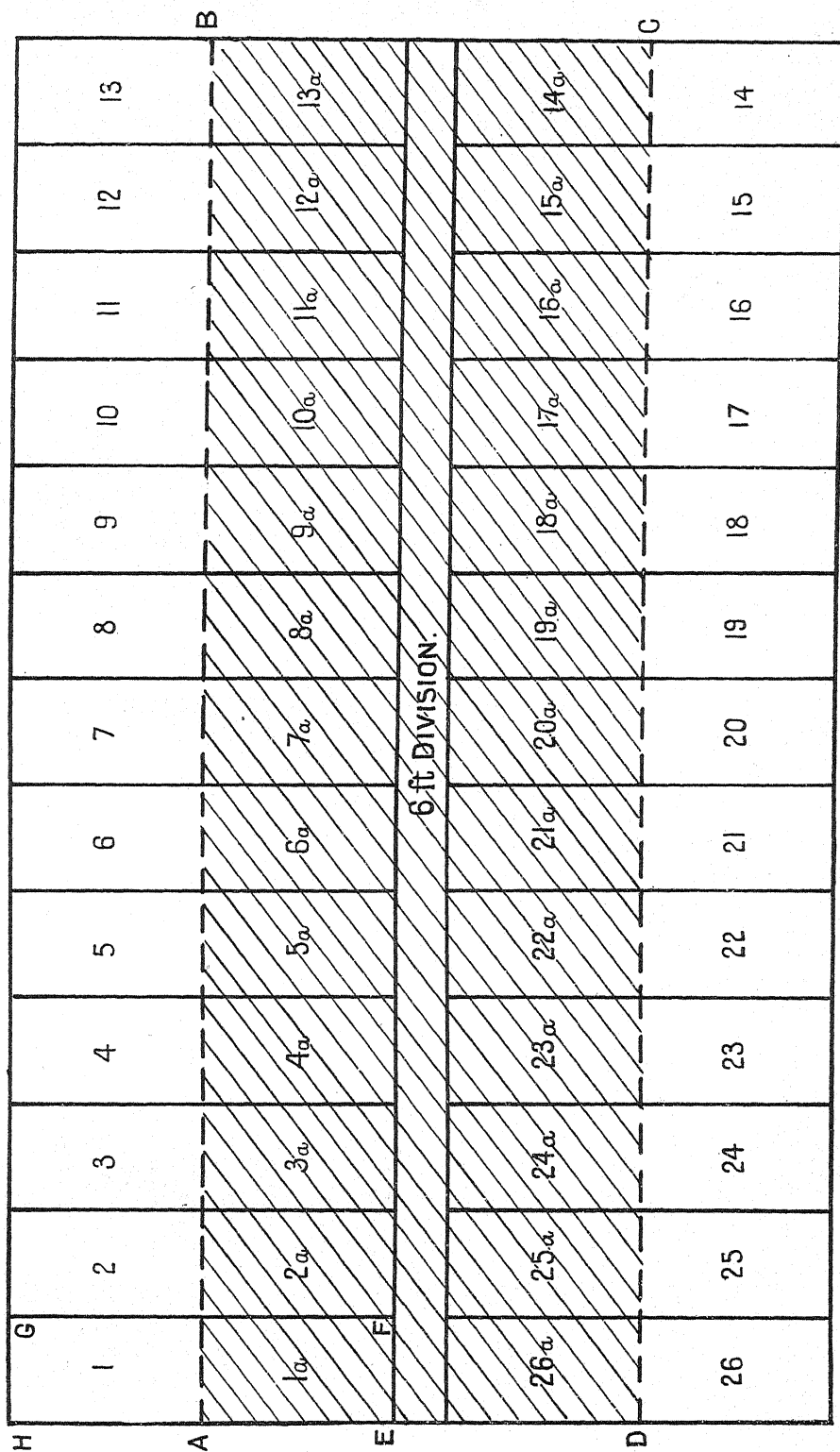


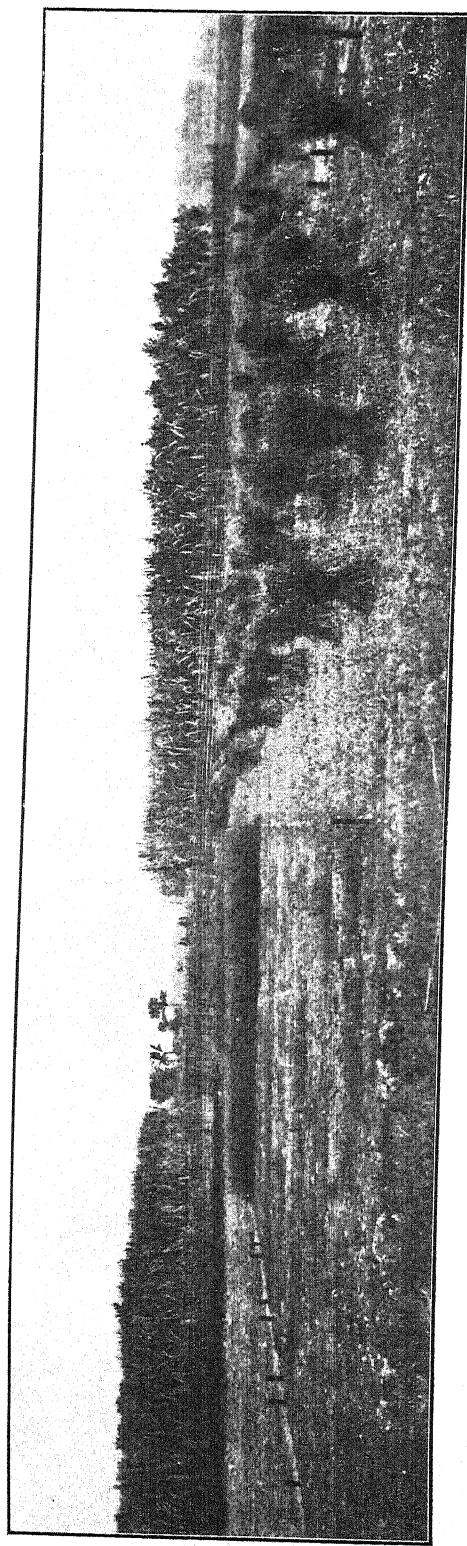
FIG. 1. PLAN OF EXPERIMENT.

Inner sub-plots 1a to 26a were limed at the rate of 30 mds. per acre. (Shaded area.)

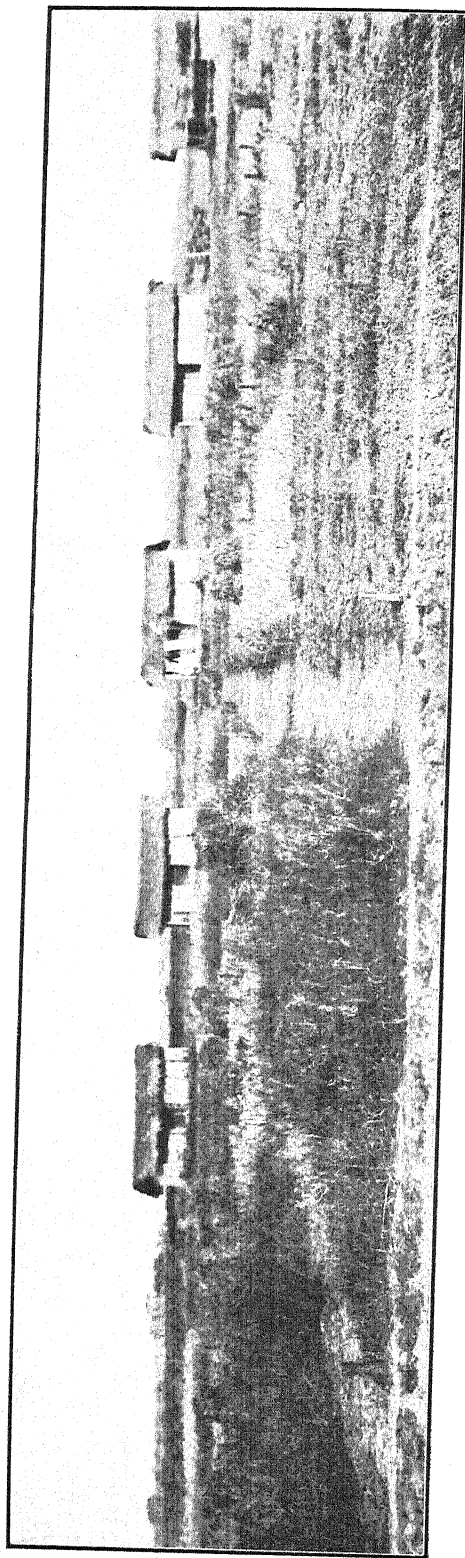
Outer sub-plots 1 to 26 were unlimed.

Area E F G H =  $\frac{1}{100}$  acre.

PLATE I.



(a)  
GENERAL VIEW OF PLOTS DESCRIBED IN THIS MEMOIR.



(b)  
SHOWING THE ACTION OF PHOSPHATE ON WEED PRODUCTION.

It is to be emphasized that in addition to the manuring as shown in the table above, the inner or "a" sub-plots each had 30 maunds slaked lime per acre.

As regards the sodium carbonate plots, the amount added was arbitrary; in view of its solubility the amounts used were thought ample for the purposes of this test, although only equal in acid neutralising power to 10 and 5 maunds good slaked lime per acre, respectively.

Potassium carbonate could not be applied in such quantities as would be necessary to supply the equivalent in neutralising power of the sodium carbonate above, chiefly by reason of the very large amount of potash which such quantities would add to the soil. It was considered sufficient to use such quantities as would supply potash in amounts respectively equal to and double that supplied as sulphate of potash in sub-plots 18 & 18a.

The flour phosphate used in plots 8 & 8a, is a very finely ground raw mineral phosphate; 85% passes a 100 mesh sieve, and it contains 25% phosphoric acid as tri-calcic phosphate, and some 23% of carbonate of lime.

The basic slag contained 20% phosphoric acid and the concentrated superphosphate 40% soluble phosphoric acid. The other artificials were of the usual average composition.

Slaked lime was applied to the inner area at the rate of 30 maunds per acre in April.

The whole experimental area was subsequently green-manured with cowpea during the rains, the more luxuriant growth being over the limed part, though the crop elsewhere was a good one. Cowpea was turned in during August, and all the other manures were applied during the third week in October in fine weather, and on nice soil moisture.

In the case of those plots receiving soluble nitrate, as it was thought desirable to have nitrate present at an early stage in the life of the plant to see whether it would prevent the death of the seedlings, the plan was adopted of applying half the nitrate just

before sowing, and the second half some weeks later as a top dressing, rather than the alternative and usual method of applying it entirely as top dressing.

All manures were evenly spread, and the plots then immediately cultivated.

No rain fell between the application of manures and sowing, which was done towards the end of October on good seed bed.

Oats was decided upon as the test crop, because up to this time this crop had invariably totally succumbed in the seedling stage, even though well manured with cowdung following green-manuring, except where moderate lime dressings or heavy application of wood ashes had been used.

In addition then to providing a sharp qualitative separation of manures, or combinations thereof, into two classes, *viz.*, those which serve to carry the crop through to maturity, and those which do not, it seemed probable that this crop would also permit of a measure of quantitative comparison between manures of the former class.

Further, it was deemed justifiable to attempt to estimate the extent of the improvement, due to manuring, in general agricultural value of the soil of each plot by the crop of oats produced, since we have evidence that many other crops, *e.g.*, soy beans, cowpeas, *jowar*, gram, linseed, *matikalai*, mustard, barley, are all considerably benefited by liming, and many of them, like oats, had entirely refused to grow in its absence.

All these crops have shown that before we can expect a really good outturn from any one of them, some base such as lime must be added to the soil, presumably to reduce acidity, and it seemed to us probable that the extent to which any manuring or combination of manuring will, either immediately or more slowly with lapse of time, effect this end, would appear to be one of the chief factors in determining its value for most field and garden crops on similar soils.



## OBSERVATIONS DURING GROWTH.

Germination was very uniformly good on all plots and was complete by November 2nd ; subsequent to sowing rain fell on the following dates, November 1st, 2nd, 3rd and 24th, December 8th, 16th, 17th, 20th, 25th, 28th.

*November 6th.*—All plots were looking well and normal.

*November 18th.*—The limed plots were all growing normally. Sub-plots 20a, 21a, 22a, 23a and 26a being then the best, followed closely by 8a, 9a, 10a, while 13a was the poorest distinctly.

The unlimed plots were in many cases already turning yellow and dying off, the phosphate plots being at the time slightly better than the average, while the sulphate of ammonia and calcium chloride plots were manifestly worse.

*December 18th.*—The general effect was most striking. All the limed plots were carrying healthy looking crops, while on the unlimed plots the plants had already quite died out in many cases, viz., on sub-plots 4, 11, 12, 13, 14, 15, 16, 17, 18, 19, 21, 23, 24, 25.

Of the remainder of the unlimed plots only those which had received additions of a basic character, viz., plots 1, 2, 3, 5, 6, 7, 8, 9 were carrying anything worthy the name of a crop, but even in these cases they did not, with the possible exceptions of plots 1, 8, 9, at all compare with the crop on the limed ends.

On sub-plots Nos. 10, 20, 22 and 26 some of the seedlings had died off, but the stronger ones were still struggling.

It will be noticed that the latter four plots had all in common received phosphoric acid. Phosphoric acid had also been applied to sub-plots 21 and 23, but in these two cases in conjunction with sulphate of ammonia as the source of nitrogen.

The previous death of the crops then on these two plots can only be ascribed to the toxic effect of the sulphate of ammonia, in the absence of lime. It is to be noted that the limed ends of the

same plots, *viz.*, sub-plots 21a, 23a were quite as good at this time as sub-plots 20a and 22a, on which the source of nitrogen was nitrate of soda.

At this time the most clearly outstanding feature was the action of lime, followed by that of the other applications of a basic character.

Phosphoric acid even as superphosphate, in the absence of lime, was exercising a very slight positive effect apparently, but was far more potent where applied in a basic insoluble form.

Potash seemed to be without any effect at present, except where used as the alkaline carbonate.

Nitrate nitrogen alone in the absence of lime had no effect, but appeared to increase that of superphosphate when the two were used together.

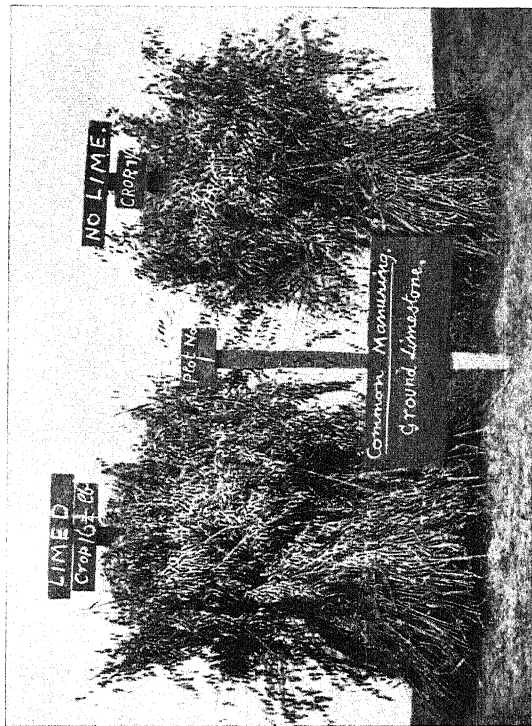
Sulphate of ammonia had killed off its crop earlier than it had succumbed on the plots receiving no manure at all, and in addition appeared to absolutely negative the slight positive effect of phosphoric acid.

Sulphate of lime had apparently no effect whatever, while calcium chloride appeared to be definitely toxic.

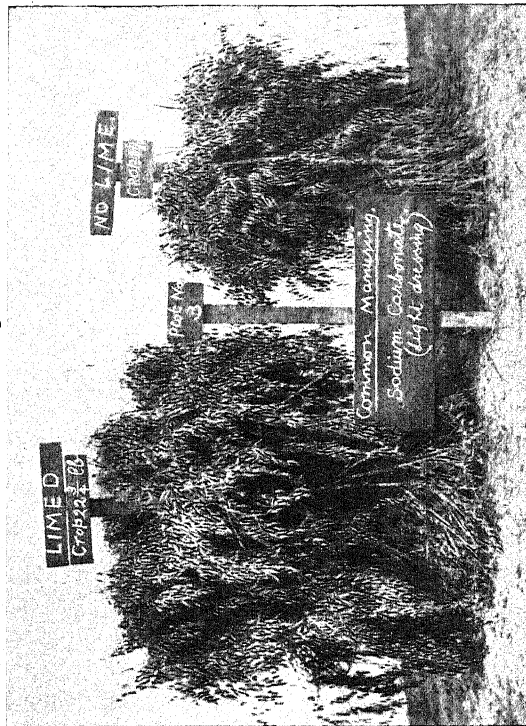
On December 19th the remaining half of the various nitrate dressings was applied to sub-plots 14, 14a, 15, 15a, 16, 16a, 20, 20a, 22, 22a, 24 and 24a, the first dose having been given previous to sowing for reasons stated earlier.

*February 24th.*—By this time the limed sub-plots were ripening off. All the plots to which had been applied phosphoric acid in any form, in addition to lime, *viz.*, 8a, 9a, 10a, 20a, 21a, 22a, 23a and 26a, were fully ripe and were cut and stooked on this date. The other lime plots were about a fortnight later in ripening off.

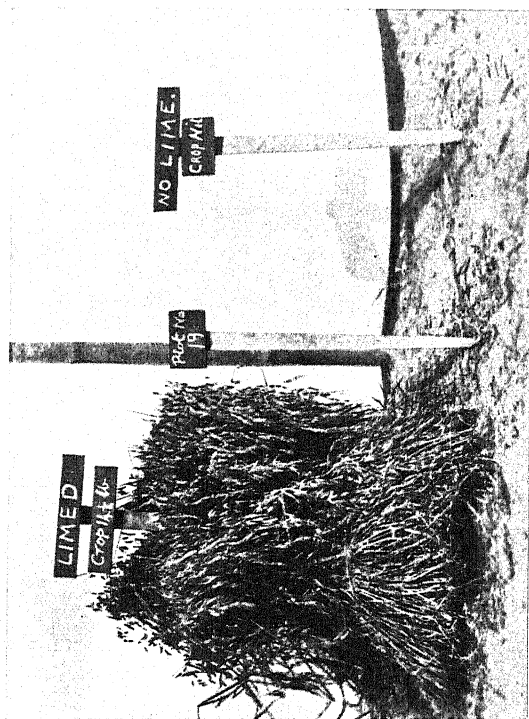
Such of the unlimed sub-plots as had carried their crops through, were the latest to ripen, some of them not ripening until a month later than this date.



Plots 1 & 1a. Common manuring - Ground Limestone.



Plots 3 & 3a. Common manuring - Sodium Carbonate, light dressing.



Plots 19 & 19a. Common manuring - Nil



Plots 5 & 5a. Common manuring - Magnesium Carbonate.



Speaking generally at this time the indications were qualitatively the same, but much more pronounced than on December 18th.

The effect of the top dressing of nitrate was *nil* on the non-limed halves of such plots as received it, except that in the cases of sub-plots 20 and 22, *i.e.*, where used with phosphoric acid, it produced a fair improvement in the crop. These plots are now forming some grain, though many plants are stunted and may not do so.

Phosphoric acid, even as superphosphate, would appear to have exercised a small but distinct ameliorating effect throughout the experiment, especially where reinforced by nitrate. This has been marked on the oats, but was particularly evident at this time in the growth of bottom weeds.

Thus, comparing the unlimed sub-plots, all those which had phosphoric acid were now carrying a thick bottom crop of weeds. This was not due to the thin crop of oats present, because other unlimed plots with no oats at all surviving were moderately free from weeds also. (See Plate I (b).)

Again, though the use of sulphate of ammonia along with phosphoric acid sufficed to kill the oats, it by no means affected the luxuriance of the weed growth.

Where used alone, however, sulphate of ammonia proved too toxic even for weeds, sub-plot 11 being absolutely bare of all vegetation whatsoever, indeed this sub-plot was undoubtedly by far the most toxic in the whole of the experimental area.

The crop from each plot was cut and stooked as it became ripe, and allowed to dry on the plot, being finally weighed.

No separation into grain and straw was attempted as in almost all cases some of the grain was eaten by rats during drying off.

Table II shows at a glance the manuring of each sub-plot and the weight of crop harvested.



Plots 26 & 26a. Common manuring - Superphosphate Sulphate of Potash.



Plots 10 & 10a. Common manuring - Superphosphate

TABLE II.

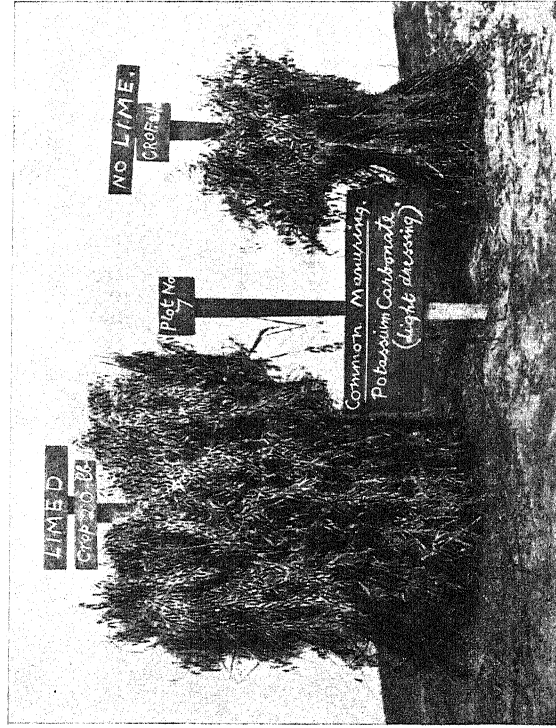
*Final outturns of plots (grain and straw.)*

Plot.	Manure used.	Unlimed sub-plot.	Limed sub-plot.
		lbs.	lbs.
1 & 1a.	Ground limestone .. ..	7½	16¾
2 & 2a.	Sodium carbonate. Heavy dressing .. ..	4	24
3 & 3a.	Sodium carbonate. Light .. ..	6½	22¾
4 & 4a.	<i>Nil.</i> .. ..	<i>Nil.</i>	16
5 & 5a.	Magnesium carbonate .. ..	6½	16¾
6 & 6a.	Potassium carbonate. Heavy dressing .. ..	7	19½
7 & 7a.	Potassium carbonate. Light .. ..	2½	20
8 & 8a.	Flour phosphate .. ..	7½	15¾
9 & 9a.	Basic slag .. ..	7	17
10 & 10a.	Superphosphate .. ..	¾	15
11 & 11a.	Sulphate of ammonia .. ..	<i>Nil.</i>	13½
12 & 12a.	Sulphate of lime .. ..	<i>Nil.</i>	13
13 & 13a.	Calcium chloride .. ..	<i>Nil.</i>	10
14 & 14a.	Sodium nitrate .. ..	<i>Nil.</i>	17½
15 & 15a.	Potassium nitrate .. ..	<i>Nil.</i>	18
16 & 16a.	Calcium nitrate .. ..	<i>Nil.</i>	16½
17 & 17a.	Muriate of potash .. ..	<i>Nil.</i>	20¾
18 & 18a.	Sulphate of potash .. ..	<i>Nil.</i>	18
19 & 19a.	<i>Nil.</i> .. ..	<i>Nil.</i>	14½
20 & 20a.	{ Sodium nitrate .. .. Superphosphate .. .. Sulphate of potash .. .. Sulphate of ammonia .. ..	5¾	21½
21 & 21a.	{ Superphosphate .. .. Sulphate of potash .. .. Sodium nitrate .. ..	<i>Nil.</i>	20
22 & 22a.	{ Superphosphate .. .. Sulphate of ammonia .. ..	4½	19½
23 & 23a.	{ Superphosphate .. .. Sodium nitrate .. ..	<i>Nil.</i>	18
24 & 24a.	{ Sulphate of potash .. .. Sulphate of ammonia .. ..	<i>Nil.</i>	19
25 & 25a.	{ Sulphate of potash .. .. Sulphate of potash .. ..	<i>Nil.</i>	17½
26 & 26a.	{ Superphosphate .. ..	2½	23

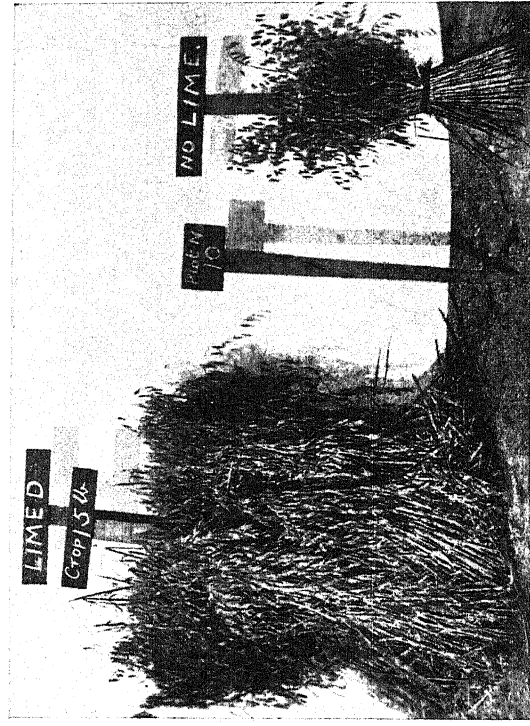
The results are striking, and taken in conjunction with our earlier experience and various observations made throughout the growing period, appear to warrant certain very definite deductions.

All the limed sub-plots produced crops, varying somewhat in magnitude, the smallest yields resulting from the use of calcium chloride or sulphate in addition. The biggest crop, strange to say, occurred in sub-plot 2a which had the heavy dressing of sodium

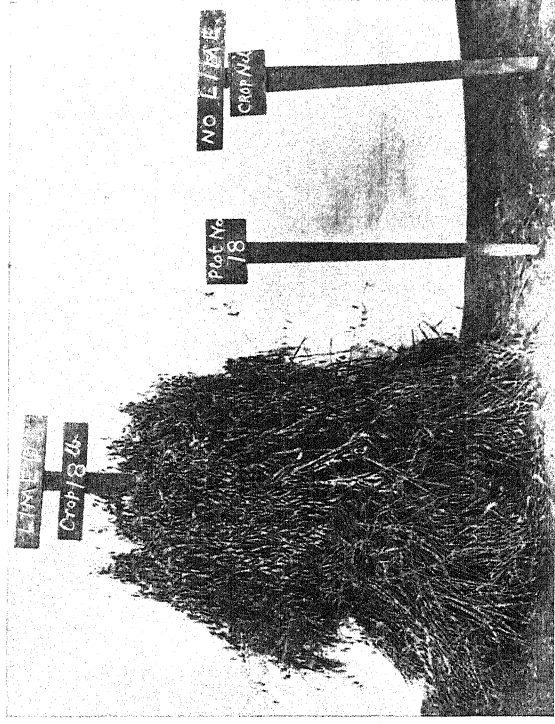




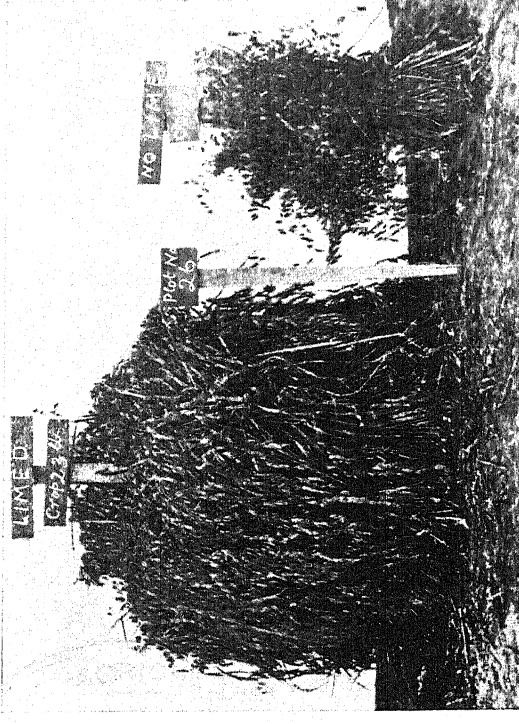
Plots 7 & 7a. Common manuring - Pot. Carbonate, light dressing



Plots 10 & 10a. Common manuring - Superphosphate



Plots 18 & 18a. Common manuring - Sulphate of Potash (supplying the same quantity of Potash as applied in basic form to Plots 7 & 7a).



Plots 26 & 26a. Common manuring - Superphosphate  
Sulphate of Potash.



carbonate as well as lime. In the absence of the latter, this large dose of sodium carbonate appeared throughout the experiment to be less beneficial than the smaller dressing, and the result confirms this. It had a marked de-flocculating effect on the surface soil. With lime, this result becomes reversed; the average superiority in the latter case, of these sodium carbonate plots over many of the other limed plots, may be due to precipitation of the lime as carbonate in a very fine state of division in the soil. It is not desirable to lay much stress on the comparatively small variations between the yields of the various limed sub-plots, as there will be seen to be a difference of some 10% in crop between the two otherwise unmanured plots 4a and 19a, and further, wet weather necessitated some of the crops standing in the field a considerable time before weighing, resulting in some loss by rats here and there.

The chief interest of the experiment lies elsewhere. *Thus, of all the unlimed sub-plots, the only ones to carry a crop to maturity at all were the whole of those to which basic manures had been added on the one hand, and on the other four plots in which superphosphate was the only constant manurial factor.*

On the face of it, it seems extremely improbable that the favourable action of lime, sodium carbonate, potassium carbonate and magnesium carbonate (*vide* Plates II and III) can be credited to any common attribute other than that of providing a base and thus diminishing the soil acidity, and probably rendering harmless toxic compounds which accompany it.

From the physical point of view, lime and the alkaline carbonates affect soils in very different ways, lime resulting in flocculation of the finest particles, while sodium and potassium carbonates have a de-flocculating action. De-flocculation was very marked on plot 2, which received the heavier dressing of sodium carbonate.

If therefore any large part of the favourable action of lime were due to its flocculating powers, one would not have expected

the alkaline carbonates to have the same qualitative effect on crop production that lime has.

Again, Schloesing found that sulphate of lime had a flocculating action, and yet this substance applied at the rate of 50 maunds per acre to sub-plot 12 failed to produce any crop at all.

There was no lack of soil moisture throughout the course of experiment, which makes it the more difficult to believe that altered water relationships as between soil and plant, which may follow the use of certain manures such as lime, can have played any but a very small part in the general result.

Again, if lime functioned in any considerable measure as a carrier of direct plant-food to the soil, why should the alkaline carbonates influence crop production as they do?

Further, if the demands of the crop on the soil for additional lime as plant-food were great, one would have expected a ready response in crop production from the application of 50 maunds sulphate of lime on plot 12. As a matter of fact, the seedlings died out on this plot quite early.

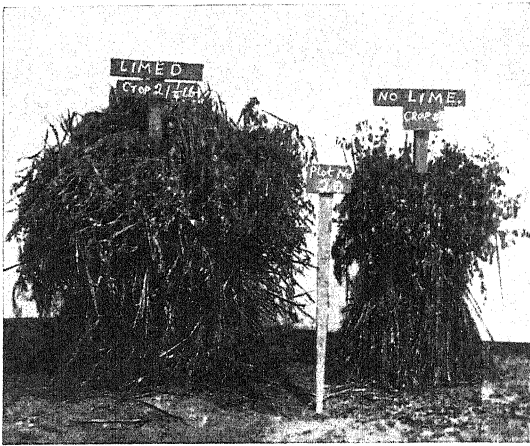
Some of these alkalis might function by virtue of their power to liberate available plant-food from the soil's reserves, *e.g.*, assimilable potash might result.

Particularly might it be argued that potassium carbonate exerted a positive effect by supplying soluble potash.

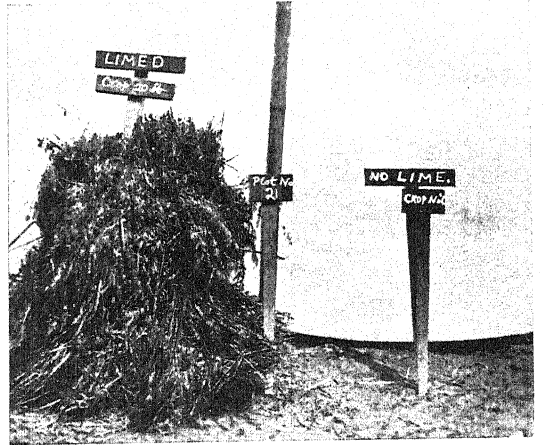
Both these arguments lose their force in that soluble potash applied as sulphate, or as muriate, to plots 17 and 18 yielded no crops whatsoever, though on plot 18 the same amount of this element of food was supplied as was given in the form of carbonate of potash to plot 7, which matured a small but measurable crop (*vide* Plate III (a) & (b)).

It has been pointed out by Hilgard and others that an amount of phosphoric acid which, in the presence of a deficiency of lime, may prove insufficient for the crops' needs in respect of this element of plant-food, may suffice when lime is present in larger quantities.

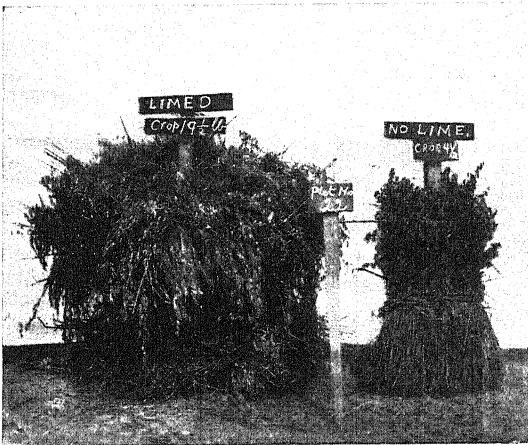
PLATE IV.



Plots 20 & 20a. Common manuring - Superphosphate  
Nitrate of Soda  
Sulphate of Potash.



Plots 21 & 21a. Common manuring - Superphosphate  
Sulphate of Ammonia.  
Sulphate of Potash.



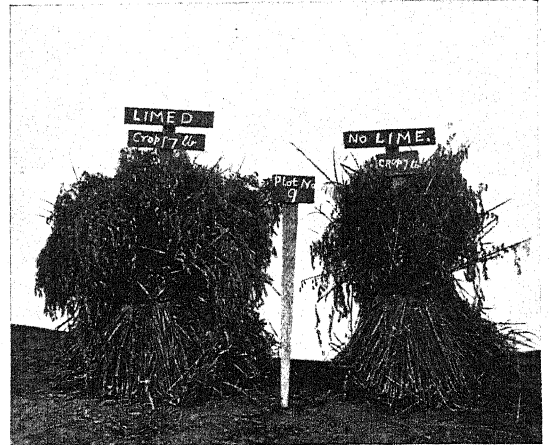
Plots 22 & 22a. Common manuring - Superphosphate  
Nitrate of Soda



Plots 23 & 23a. Common manuring - Superphosphate  
Sulphate of Ammonia



Plots 8 & 8a. Common manuring - Raw mineral phosphate.



Plots 9 & 9a. Common manuring - Basic Slag.





Undoubtedly added lime would appear to influence the availability of the soil's phosphoric acid content as measured by solubility in 1% citric acid solution, as is shown by the following figures obtained recently from field plots variously limed.

	Per cent. $P_2O_5$ soluble in 1 % citric acid by the method of Dyer.
Unmanured plot .. .. .	·0048%
Bone meal „ .. .. .	·0055%
Lime plot 30 mds. per acre .. .. .	·0069%
Lime 30 mds. & bone-meal plot .. .. .	·0087%

This aspect of the action of lime is further borne out by some experimental crop results in the field using insoluble forms of phosphate with and without lime.

Bearing in mind then the beneficial action observed throughout this experiment to follow the use of phosphoric acid in any form, it is quite conceivable that the action of lime may in part be due to some increase in the availability of the existing phosphoric acid supplies of the soil.

As will presently appear, it seems highly probable that the favourable action of phosphoric acid is not to be entirely explained on the ground that it acts merely as a plant-food; by its action on the physiological processes of the root system generally it may assist indirectly in reducing the amount of toxic material in the soil.

The arguments advanced by O. Loew in regard to the physiological significance of establishing certain ratios of lime to magnesia, are clearly incapable of explaining the early observed effect of lime on this soil, since the alkaline carbonates produce a measurable result in the same direction, and, moreover, the effect on crop production is the same, whether the ratio of magnesia to lime is widened by using magnesia or narrowed by using lime, *so long as both are applied in a basic form* (Plate II).

H. B. Hutchinson<sup>1</sup> has pointed out that caustic lime may bring about a measure of partial soil sterilisation, his conclusions being based on tests in which, in the main, heavy dressings of lime were used up to 6.6 tons per acre.

If it be contended that any large part of the beneficial effect of lime on the Jorhat soil is due to partial sterilisation, it is necessary to assume that the other basic dressings used in our experiments also acted in the same way, and at present there does not seem to be any evidence that a dressing of potassium carbonate of 164 lbs. per acre (plot 7) would effect any appreciable amount of partial sterilisation.

From the purely biological point of view, in view of all the evidence which is to be found in literature that acidity definitely retards the work of nitrifying and other soil bacteria, promoting rather the development of moulds, leading to a decline in fertility; and though no special study has been made in connection with this experiment of possible changes in bacterial activity, it is impossible to resist the conclusion that the normal functioning of soil bacteria generally on these soils only becomes possible as a result of early chemical changes following the direct use of a base such as lime.

Nitrification, though greatly reduced, still goes on slowly in acid soils, but is increased by liming, as shown by Hall.<sup>2</sup>

That it is so increased by liming has all along seemed evident in the improved colour of cropping in our various experiments.

The increase in nitrate production, in addition to adding to the food-supply of the plant, would as shown by Schreiner and Reed,<sup>3</sup> further assist the lime in promoting root oxidation, which is followed by a reduction of toxicity due to certain organic toxic soil compounds.<sup>4</sup>

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<sup>1</sup> *Journal of Agricultural Science*, Vol. V, Part 3.

<sup>2</sup> *Nitrification in Acid Soils*. Hall Miller Gimmingham, *Proc. Roy. Soc.*, Vol. 80.

<sup>3</sup> *Bot. Gaz.*, 47, 355.

<sup>4</sup> Schreiner and Skinner. *Ibid*, 50, 161.

That the direct addition of nitrates to the soil on plots 14, 15 and 16 did not result in keeping the crop alive in those cases in the absence of lime, does not disprove this observation in regard to the destruction of toxins incident on improved root oxidation, since the showers which fell after sowing may have largely removed the nitrate beyond the reach of the young roots, and the seedlings were already dead before the second application of nitrate could be made.

Again, even though it had exercised its full effect, it is conceivable that added nitrate may not, in the absence of other contributing agencies, have sufficed of itself to diminish the toxicity sufficiently to enable the crop to survive.

In support of this contention the increase in crop production due to superphosphate without lime, when re-inforced by nitrate of soda, may be cited, this result being reversed when sulphate of ammonia was used, *c.f.*, Plate III (c) with Plate IV (c) & (d).

It is necessary at this stage to consider the rôle which phosphatic manures in the absence of lime have played in the experiment. It was previously pointed out that, of the non-limed series, among the few plots on which the seedlings survived and which matured any crop at all, were four in which superphosphate formed the only common manurial factor.

Phosphoric acid was applied alone in basic form to plots 8 and 9, and as acid superphosphate alone to plot 10, this being reinforced by other manures on plots 20, 21, 22, 23 and 26.

The results show that plots 8 and 9 (Plate IV (e) & (f)) receiving raw phosphate and basic slag respectively gave the biggest crop of the whole phosphate series, only approached, but not equalled, by superphosphate when used along with nitrate of soda and sulphate of potash on plot 20.

Neither the raw phosphate nor the basic slag supplied sufficient lime to neutralise any but a small part of the acidity of the first three inches of soil, which remained quite acid in reaction. Their favourable action on crop production is, therefore, no doubt jointly

due to their basic character and to the fact that they supply available phosphoric acid. It is, however, quite impossible to divorce these two aspects in the case of these two manures, and thus a consideration of the superphosphate series becomes necessary.

In the absence of lime, superphosphate alone (plot 10) matured a very small short crop; this was increased by the addition of sulphate of potash (plot 26) or nitrate of soda (plot 22), the latter giving the bigger increase, while the largest crop of the series resulted from plot 20 which had both nitrate and potash in addition to superphosphate (Plates III (c) & (d), and IV (a) & (c)).

In those cases, plots 21 and 23, in which nitrogen was supplied as sulphate of ammonia, the result so far as the oats crop was concerned, was the absolute negation of the beneficial effect of the superphosphate.

It will be seen then, that the use of acid superphosphate has a small qualitative effect on crop production similar to that exercised by lime, and the other basic manures used.

To what are we to ascribe this action? It were unnecessary to point out that it cannot neutralise acidity; at best it can but add a certain amount of sulphate of lime which, as we have seen, has absolutely no effect.

It adds to the soil a certain amount of freely available phosphoric acid, but it does so whether used alone or with nitrate of soda or with sulphate of ammonia. There is no reason to suppose that sulphate of ammonia could in any way affect its action as a source of available phosphoric acid to the plant.

The net effect of using sulphate of ammonia in addition is, however, detrimental by virtue of the increase in soil acidity which follows its use.

In view of the deficiency of phosphoric acid in the soil, it must be granted that superphosphate would function partly as a direct plant-food, providing the general soil conditions are such as to permit the plant to survive.

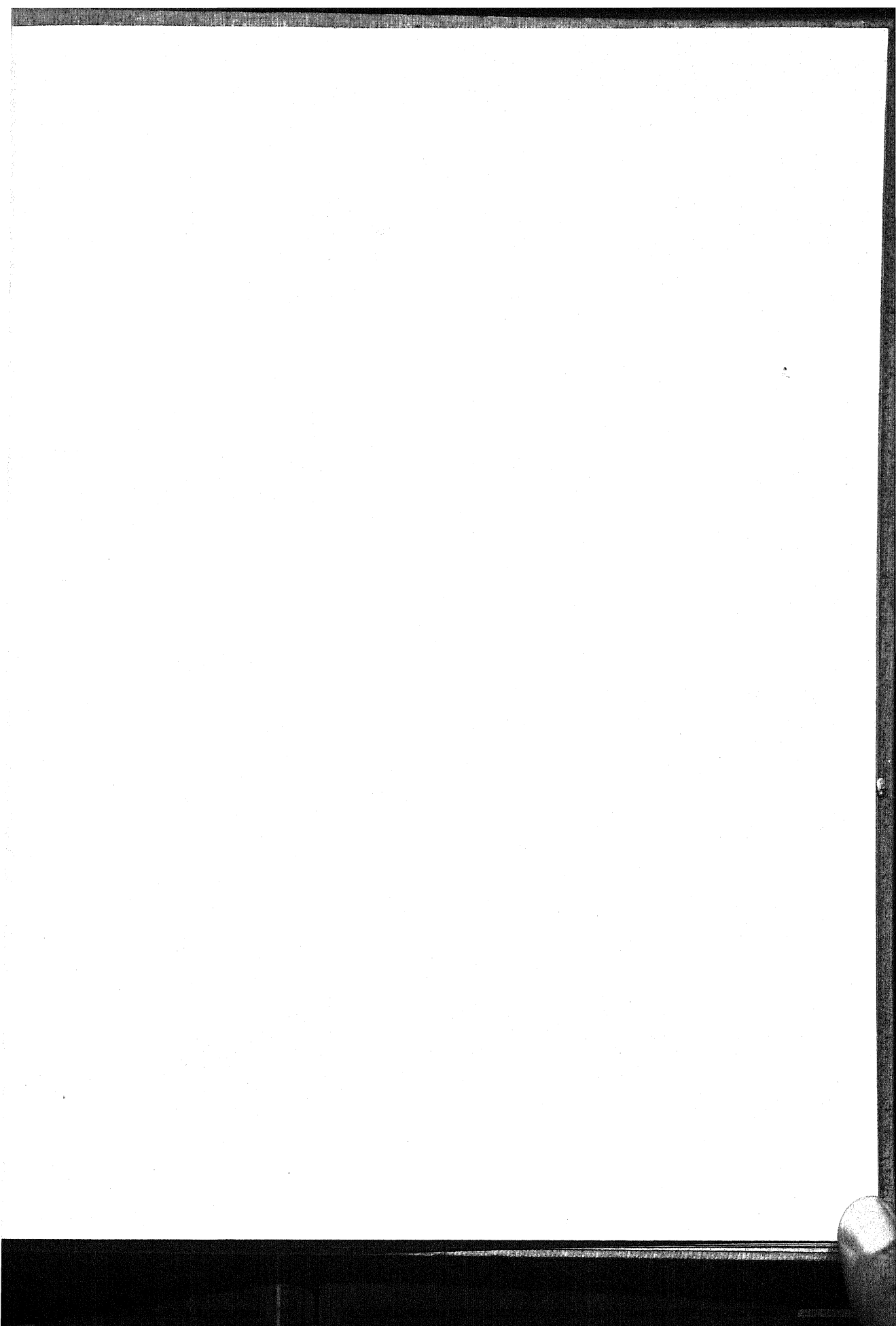
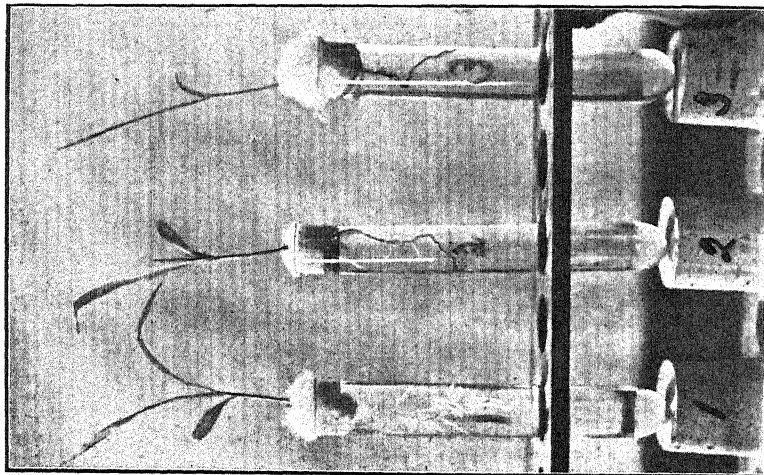
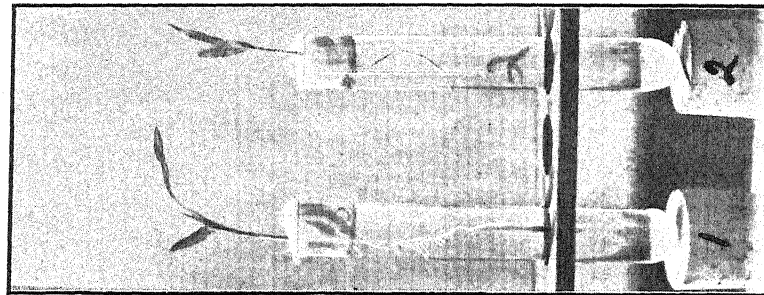


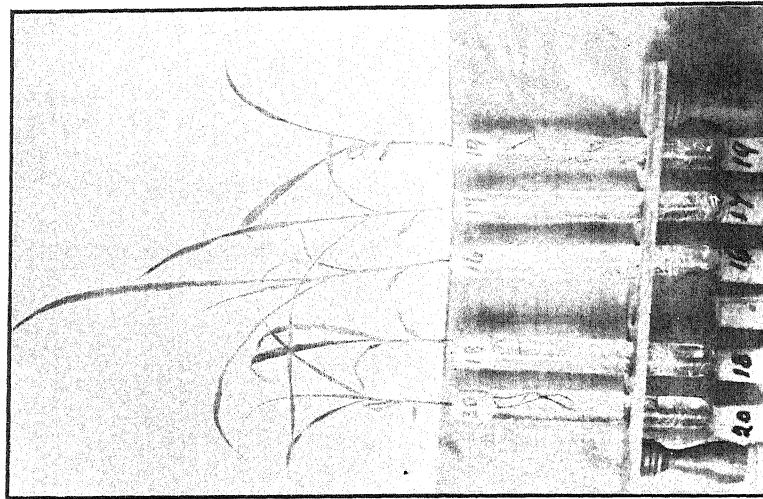
PLATE V.



(a)



(b)



(c)

JOWAR SEEDLINGS.



But this function is probably not its only one ; by its power to stimulate the root system in the early stages of growth as pointed out by Russell<sup>1</sup> whereby among other things the extra-cellular root oxidation would probably be increased, leading to destruction of toxic material, the survival of the plant might be rendered possible.

Schreiner and Reed<sup>2</sup> show that the roots of plants do exhibit an extra-cellular oxidising power in nutrient solutions, and that phosphates usually produced material increases in the oxidation in solutions to which they were added ; further, their experiments showed that " plant roots are able to oxidise a certain amount of deleterious organic material, and that the presence of salts which favour oxidation increase the ameliorating action of the plant."

Experiments on *jowar* seedlings in culture solutions of the toxin<sup>3</sup> extracted from the Jorhat soil, also showed that the addition of phosphate materially reduced the toxic effect on the plant.

It may be stated here that the most marked effect of this toxin was on the young roots ; their growth was at once stopped, the root became discoloured, generally hooked round and sometimes swelled up at the end, leading to the death of the plant within a short period. These effects were considerably modified by the addition of phosphate, especially where the toxin concentration was low ; discolouration was nearly absent and lateral roots were formed. Moreover, it is interesting to note that where 5 c.c. of a complete nutrient solution was added to the toxin solution, the effect of the latter, though still apparent, was still further diminished, again, especially so where the toxin was present in least concentration. (Plate V.)

This comparative behaviour of *jowar* in the presence of the soil toxin in tube cultures, using on the one hand a complete nutrient solution and on the other one containing only phosphate, again

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<sup>1</sup> Russell " *Soil Condition and Plant Growth*," pages 36 and 37.

<sup>2</sup> *Bull. 56, Bur. of Soils, U. S. Dept. of Agri.*

<sup>3</sup> The record of the work on this toxin will be published separately—A. A. M.

accorded well with the growth of oats in the field, *vide* plots 10 and 20, in the absence of lime. (Plates III (c) and IV (a)).

It is obvious that while superphosphate cannot bring about any effects by neutralisation of acidity in the way that lime can, in view of the evidence adduced above, its action may probably be in part due to a destruction of organic compounds which are specifically toxic, whose presence or accumulation is probably only possible in sour soils deficient in basic ingredients, but whose destruction may be brought about by such treatment of, or addition to, the soil as stimulates oxidation, whether by the roots or other biological agencies.

Part, if not the whole, of the noxious matter of our soil is acid, but on many grounds it is unreasonable to suppose for a moment that the entire acidity of the soil or, indeed, any but a very small part of it, is made up of acids which are specifically toxic, in the way that the hydroxystearic acids are, for instance.

No method of determining what part of the acidity may be due to acids specifically toxic has yet been devised, as the methods of isolation employed are not quantitative, so it is impossible to say in any given case what part of the acidity is due to specifically toxic acids and what is not. But, on the reasonable assumption that the total acidity is the sum of two factors, one specifically toxic and the other not, then the superior action of lime on crop production may be explained on the ground that, directly or indirectly, it leads to the destruction of both factors, thus establishing better soil conditions than may follow a temporary diminution in the amount of specifically toxic material alone, which may be brought about by superphosphate, but which is sufficient to permit of some growth even in the presence of the remaining acidity.

That the sum total of soil acidity is commonly not due to specifically toxic acids is further borne out by a statement by Storer<sup>1</sup> to the effect that fairly good crops of oats, amongst

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<sup>1</sup> *Agriculture*, Vol. 11.

other crops, are grown on many German moors which exhibit a strong acid reaction, both as regards surface and sub-soils.

However, the presence, in excess of a certain amount of acids which are not specifically toxic in themselves, may prevent crop production as is proved by a comparison of plots 10 and 23 (Plates (c) and IV (d)). The addition of sulphate of ammonia on the latter plot, to the superphosphate used in both, though supplying nitrogen, increases the general acidity by leaving a residue of sulphuric acid, which may inhibit to some extent the increased root oxidation which would follow on the use of superphosphate alone, since Schreiner and Reed observed that the activity of the peroxidase produced by roots is somewhat inhibited by the presence of acid, being greatest in neutral or slightly alkaline solutions; and again, of course, normal bacterial acidity is reduced with increase in soil acidity.

That the beneficial action of the superphosphate was entirely inhibited, however, by addition of sulphate of ammonia seems to be unlikely in view of some observations made on the growth of weeds on these plots in general.

More or less weed growth (chiefly grass) was apparent on all the non-limed plots, with the exception of plot 11, which had sulphate of ammonia alone; this plot was absolutely bare even of weeds.

Plots 21 and 23 (superphosphate and sulphate of ammonia) were covered with a luxuriant growth of weeds, but no oats. (Plate I (b)).

It will be seen then that sulphate of ammonia used alone had such an effect in general as to render the soil incapable even of weed production in the cold weather. The power, however, to grow weeds was restored and the weeds grew more luxuriantly than ever, when superphosphate was used in addition.

Though this increased vigour of weed growth may be due to the phosphoric acid acting as direct plant-food, the restoration

of the power to produce weeds at all can, it would seem, have no connection with direct food action, as the ability to grow weeds is equally ensured by withholding the ammonia sulphate in the first instance, in the absence of any direct addition of phosphoric acid.

The restoration of this capacity to produce weeds effected by superphosphate after the use of sulphate of ammonia, may then be due to its power to bring about some diminution in toxic content, which, though not sufficient to yield any oats, is quite enough for the purposes of weed growth.

It is not unreasonable to suppose that improved processes of oxidation, whether by the roots themselves or following on increased bacterial activity, will result in the partial or complete destruction of toxic compounds.

Some of these compounds, already isolated and identified by Schreiner and his associates, have proved to be easily oxidisable compounds, which a study of their chemical constitution would premise.

Further, the toxin solutions used in the author's experiments with *jowar* seedlings, after mere exposure in a flask to light and air for several weeks, were very largely deprived of their toxicity thereby.

A consideration of the following facts :—

- (1) that the mere use of lime renders crop production possible, being especially effective when used in sufficient quantity to render the surface soil neutral or faintly alkaline ;
- (2) that superphosphate has a similar qualitative effect, apparently much smaller than that of lime, but becoming greater when reinforced by nitrate of soda ;
- (3) that toxic organic compounds capable of being destroyed by oxidation are present in the soil ;

- (4) that lime, nitrates, phosphates are all able to promote biological oxidation, whether by the plant roots themselves or by other biological agencies,

would lead to the conclusion that the ability of this soil to produce certain crops is dependent on the diminution of toxic agencies present; that the more complete the destruction the bigger the crops will be, but that the best results only follow on an entire elimination of acidity, whether due to specifically toxic compounds or not; the latter observation would explain the very much more marked action of lime, as opposed to that exercised by superphosphate, which is clearly proved by the fact that though the use of sulphate of ammonia is able to completely negative the effect of superphosphate so far as the production of oats is concerned, its addition with previous liming is followed by no such consequence, though, even in this case, one would hesitate to say that its use has proved beneficial, *c.f.*, sub-plots 4*a* and 19*a* with 11*a*; 18*a* with 25*a*; 26*a* with 21*a*; also 10*a* with 23*a*. Only in the last case, *i.e.*, where sulphate of ammonia is added to superphosphate, in the presence of lime, is an increase registered from its use. On the contrary, it is interesting to note here that similar comparisons amongst the nitrate of soda-limed plots come out in favour of the nitrate in every case but one.

It would appear that toxic compounds have not been found to be definitely associated with any soils but such as are sour, often badly aerated, and deficient in calcium carbonate. It does not follow therefrom that all sour soils harbour specific toxins.

While any degree of acidity is more or less harmful on biological grounds to many cultivated plants, the case becomes greatly aggravated when such acidity is partly due, as in the Jorhat soil, to specifically toxic organic compounds. These compounds owe their continued presence in dangerous amounts in the soil to the impairment of oxidation processes which follow on the establishment of acid conditions in soils deficient in basic ingredients. A reduction in the amount of the toxic compounds merely, such as

may follow the use of superphosphate and other fertilizers, can only be a temporary measure and does not cut at the root of the evil. The general conditions which originally gave rise to toxin formation still remain. Something more is necessary, and these experiments show, I think, that for the best results, the addition of a basic substance such as lime is clearly necessary, while other experiments being made point to the fact that sufficient base must be used to completely neutralise the soil, at any rate to cultivation depth, and periodical additions will be necessary to prevent a relapse into sourness. Infertility in a soil is not, in many cases, a mere negative property, but is often due to the presence of an overwhelming positively injurious factor. Alter or remove this factor, and all the elements of fertility will frequently be found to be present. Greig Smith<sup>1</sup> records the case of a soil which was very toxic, becoming normal after heavy rains due to washing down of the toxin into the lower layers.

The work on partial soil sterilisation at Rothamsted, also that of Schreiner and his associates on soil organic matter, show that it is undoubtedly true that the soil, both in regard to its hosts of living organisms as well as the chemical compounds present, may harbour mutually opposing factors, and that soil fertility varies as the balance between them changes or is deliberately altered.

This balance may be varied by cultivation, manuring, the use of lime, cropping and the rotation of crops, as well as by partial sterilisation by heat or antiseptics.

The harmful factor is certainly in the ascendancy in the Jorhat soil, and lime clearly seems to be the most effective agent in bringing about a change for the better.

Schreiner and Lathrop<sup>2</sup> referring to toxic soils of low oxidising power observe that "liming, drainage, and the application of good organic manures are the most potent factors in promoting oxidation in soils. Liming has been found to be very beneficial,

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<sup>1</sup> *Centr. Bakt.*, June 22, 1912.

<sup>2</sup> *Bull. 80. Bur. of Soils, U. S. Dept. of Agriculture.*



aiding the destruction of harmful bodies of this nature, both by combining with them and also by oxidising them to other less harmful or even beneficial compounds. Drainage also aids materially in two ways ; first, it allows a freer access of air with deeper penetration of healthy roots, which in time promotes oxidation and thus aids the destruction of organic matter ; secondly, it produces beneficial results by an actual removal of the harmful material in the drainage waters, as well as perhaps eliminating the cause of its formation. The addition of good organic manures will also assist in the destruction of the compounds already in the soil. The introduction of easily decomposed organic matter causes greater bacterial activity and greater oxidation in the soil, so that through the inauguration of the processes of its own decomposition, it has the effect of causing the changes in the organic matter in the soil to proceed in a different direction from that which formerly existed. The fertilizer salts are shown by experiments to act in a very similar manner, inducing or quickening changes which take place without them only very slowly or not at all." Our general experience at Jorhat bears the above out very strongly, and our experiments show that either as regards intensity or permanence of effect, lime is clearly unapproached by any ordinary combination of manures.

Its functions are such as are obviously shared by other basic substances, and whatever other changes may follow later, there can be no doubt that its effect depends primarily upon its power to neutralise acidity and to destroy toxic material. At the same time, the use of caustic lime may lead to a diminution of protozoal content and activity ; in the result, oxidation processes are improved, a great impetus is given to the activities of soil bacteria, the improved bio-chemical factor leads to the production of compounds beneficial to plant life, and fertility results.

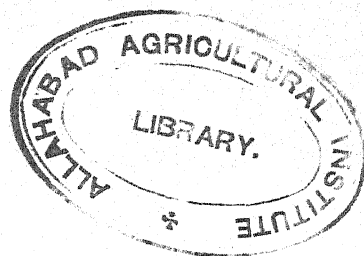
Since the foregoing was written, the 2nd year's crop of oats has been sown and is now in ear ; the results confirm very closely those of the first year, and at present suggest no modification whatever of the conclusions which have been drawn therefrom.

One point worthy of special mention is that one of the unlimed and otherwise untreated plots was watered daily from the time of germination. This had not the slightest effect on the survival of the crop, which died out as usual in the seedling stage.

This disposes finally of any contention that the crop fails to survive for want of moisture, and also that the action of lime is in any way connected with any effect it might have on the supply of water to the plant by the soil.

Other points which might also be briefly mentioned are as follows :—

1. Plot 1 (ground limestone) is a great improvement on last year.
2. Plots 2, 3 (sodium carbonate) are again cropping, with No. 2 better than No. 3 in the second year.
3. Plots 6 and 7 (potassium carbonate) are almost bare ; the effect of small initial dressings of soluble alkali carbonates is evidently very transitory.
4. Plot 5 (magnesia carbonate) is equal to last year.
5. A new plot, to which an excessive quantity of superphosphate was applied (160 lbs. sol.  $P_2O_5$  per acre), points to the conclusion that the use of excessive amounts of acid superphosphate, in the absence of lime, is detrimental, presumably by virtue of the extra acidity added to the soil.



## EXPLANATION OF PLATES.

### FRONTISPIECE.

Jorhat Farm. Block G.

The plots on the left were limed, those on the right unlimed ; treatment is otherwise identical. Oats and gram were sown across both areas. Observe the standing crops of both on the limed side, and the absolute failure on the other.

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### PLATE I.

- (a) General view of plots described in this paper. Compare the crop on the limed ends of the plots (right side of picture), with that on the unlimed ends (left side).
- (b) Showing the action of phosphate on weed production. The plots in the foreground to the left received superphosphate ; that on the right was unmanured.

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### PLATE II.

- (a) Plots 1 and 1a. Common manuring = ground limestone.
- (b) Plots 19 and 19a. Common manuring = *nil*.
- (c) Plots 3 and 3a. Common manuring = sodium carbonate, light dressing.
- (d) Plots 5 and 5a. Common manuring = magnesium carbonate.

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### PLATE III.

- (a) Plots 7 and 7a. Common manuring = potassium carbonate, light dressing.

- (b) Plots 18 and 18a. Common manuring = sulphate of potash, supplying the same quantity of potash as applied in basic form to plots 7 and 7a.
  - (c) Plots 10 and 10a. Common manuring = superphosphate.
  - (d) Plots 26 and 26a. Common manuring = superphosphate, sulphate of potash.
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## PLATE IV.

- (a) Plots 20 and 20a. Common manuring = superphosphate, nitrate of soda, sulphate of potash.
  - (b) Plots 21 and 21a. Common manuring = superphosphate, sulphate of ammonia, sulphate of potash.
  - (c) Plots 22 and 22a. Common manuring = superphosphate, nitrate of soda.
  - (d) Plots 23 and 23a. Common manuring = superphosphate, sulphate of ammonia.
  - (e) Plots 8 and 8a. Common manuring = raw mineral phosphate.
  - (f) Plots 9 and 9a. Common manuring = basic slag.
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## PLATE V.

- (a) *Jowar* seedlings

Tube 1 = water.

„ 2 = Toxin solution (125 pts. per million) + lime-water to neutrality.

„ 3 = Toxin solution (125 pts. per million).

Root development in tube 2, though not so good as that in water, was much greater than that in tube 3, to which no lime-water was added.

In many other similar cultures, the effect of lime in promoting root development in the presence of the toxin was always well marked.

(b) *Jowar* seedlings.

Tube 1 = water.

„ 2 = Toxin solution, concentration 80 parts per million.

The very marked repressive action of the toxin in tube 2 on root development was produced within 48 hours.

A solution of only 40 parts per million was equally effective.

(c) *Jowar* seedlings.

Tube 16 = 5 c.c. nutrient solution + water.

„ 17 = { 5 c.c. nutrient solution + toxin solution, con-  
„ 19 = { centration 100 per million.

„ 18 = { 5 c.c. nutrient solution + toxin solution, concentra-  
„ 20 = { tion 240 per million.

Nutrient solution	{	KNO <sub>3</sub>	0.5 gm.
		MgSO <sub>4</sub>	0.5 gm.
		CaSO <sub>4</sub>	0.5 gm.
		Na <sub>2</sub> HPO <sub>4</sub>	0.5 gm.
		Fe <sub>2</sub> Cl <sub>6</sub>	2 drops.

## APPENDIX.

### *A. Chemical Analysis of the Jorhat surface and sub-soils.*

				Surface soil.	Sub-soil.
				%	%
Soluble in 26 % Hydrochloric acid with 12 hrs. digestion at 100 °C	{	Phosphoric acid	(P <sub>2</sub> O <sub>5</sub> ) ..	0.025	0.020
		Potash	(K <sub>2</sub> O) ..	0.115	0.135
		Lime	(CaO) ..	0.154	0.144
		Magnesia	(MgO) ..	0.166	0.148
Soluble in 1% Citric acid with 7 days digestion,	{	Phosphoric acid	..	0.008	0.008
		Potash	..	0.007	0.011
Loss on ignition=organic matter + combined water				3.26	1.84
Nitrogen	..	..	..	0.114	0.051
Carbonic acid (CO <sub>2</sub> )	..	..	..	0.009	0.007
=Calcium Carbonate	..	..	..	0.02	0.015
Reaction	..	..	..	Acid	Acid

### *B. Mechanical Analysis (ignited fractions).*

				Surface soil.	Sub-soil.
				%	%
Fine Gravel	(3 — 1 m.m. diam)	..	..	<i>Nil.</i>	<i>Nil.</i>
Coarse Sand	(1 — 0.2 m.m. diam)	..	..	7.2	6.3
Fine „	(0.2 — 0.04 m.m. diam.)..	..	..	52.5	52.8
Coarse Silt	(0.04 — 0.01 m.m. diam.)..	..	..	22.6	17.6
Fine „	(0.01 — 0.002 m.m. diam.)	..	..	5.0	9.4
Clay	(< 0.002 m.m. diam.) ..	..	..	6.6	9.9
Moisture + Loss on Ignition .. .. .				5.1	3.1
				99.0	99.1



*C. Moisture Constants.*

				Hygroscopic Capacity.	MAXIMUM WATER-SATURATION CAPACITY.		MINIMUM WATER-SATURATION CAPACITY.		Moisture in air-dry soil.
					Per cent. of water in saturated soil by weight.	Per cent. of water in saturated soil by volume.	Per cent. of water by weight.	Per cent. of water by volume.	
Surface soil	..	..	..	3.10	31.9	50.5	11.2	13.9	1.3
Sub-soil	..	..	..	..	30.0	50.0	7.2	9.1	1.19

*D. Acidity.*

Expressed as parts quicklime (CaO) required to neutralise one million parts of air-dry soil, the acidity of the surface and sub-soils on the Jorhat Farm varies between the following limits :—

Surface soil 880—1350 parts CaO per million.

Sub-soil 650—770 parts CaO per million.

JORHAT;  
*September, 1913.* }